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A study of the recrystallization and the mechanical properties of indium

Louis John Reitsma Jr.

A STUDY OF THE RECRYSTALLIZATION AND THE MECHANICAL PROPERTIES OF INDIUM

An Abstract

of a Dissertation

Presented to

the Faculty of the Graduate School

University of Missouri

In Partial Fulfillment

of the Requirements for the Degree

Doctor of Philosophy

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by

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May 1959

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The recrystallization temperature and the mechanical properties of tensile strength, elongation, reduction in area and hardness were determined for 99.97% indium. Metallographic techniques were developed and stress rupture data were obtained.

Single crystals of indium were grown in a horizontal furnace with a traveling temperature zone, and sectioned in a strain-free manner, with an etch-cutter. Because of the low recrystallization temperature of indium, no further work was done on the single crystals.

The effect of recrystallization on electrical resistance, thermoelectric force, hardness, bending strength, crystallographic orientation and microstructure was studied. The range of recrystallization temperature for small amounts of cold work was from -40° to 0°C and for large amounts of cold work was from -110° to -70°C.

The mechanical properties were found to be as follows: hardness, 0.72 Brinell, 1.197 Knoop and 1.266 to 1.402 DPH; tensile strength 388 psi.; elongation, 70%; and reduction in area, 95%. Stress rupture data were obtained, and a master rupture was plotted for indium.

A major improvement was made in the etching procedure which employed aqua regia to show grain orientation and contrast. The use of the etch-cutter to obtain unrecrystallized microstructures was also unique.

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ACKNOWLEDGEMENTS

The author would like to thank the Indium Corporation of America for the loan of the indium used in this investigation. Thanks are also extended to the Metallurgy Department of the Missouri School of Mines and Metallurgy for the use of their equipment and the funds to build other necessary equipment.

The author is also indebted to Dr. D. S. Eppelsheimer, Professor of Metallurgical Engineering, for his assistance, support and encouragement during the course of this investigation.

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CHAPTER I

INTRODUCTION

Indium is a very soft metal with a specific gravity of 7.3 and is the only metal to crystallize in a face-centered tetragonal lattice. It usually occurs in zinc blendes, but is also found in many other ores in varying amounts, considerable quantities being available if future needs require their exploitation. Indium metal is extracted from its ores in numerous ways. Most of which involve an acid leaching operation to put the metal in solution, followed by either displacement with zinc or electroplating from the acid bath. Refining is accomplished by successively dissolving and plating with intermediate purification of the plating solution.

At present indium has very little practical application, being used to some extent for stabilizing gold in dental alloys and silver in bearing alloys, in low temperature solders and in conjunction with cadmium as a neutron detector. The only nuclear application so far has been an alloy of indium, silver and cadmium suggested as a replacement for hafnium. Some of its compounds, in particular the antimonides and arsenides, are finding application as semi-conductors. Other applications await only the necessary research to prove their feasibility.

A study of the properties of indium, in particular its single crystal properties, would be of interest in promoting its further utility, and indium because of its low melting point and good chemical stability in air is an ideal material for single crystal growth and

study. Therefore, the original problem was to be the growing and studying of indium single crystals. The first step was the construction of a crystal growing apparatus and the development of a procedure for the growth of indium single crystals.

The investigation of these crystals was complicated by the low recrystallization temperature of indium (below room temperature). To partially overcome this difficulty, a method of cutting the crystals in a strain-free manner was perfected. Further study, however, required a better understanding of the nature of the recrystallization process, particularly the recrystallization temperature. The temperature of recrystallization was determined by studying the effects of recrystallization on electrical resistance, thermo-electromotive force, hardness, bending strength, crystallographic orientation and microstructure.

While searching through the literature for the above investigation, a discrepancy was noted in the accepted value of the tensile strength and the other properties of indium. A check with the original source revealed a misinterpretation of the data and suggested a check of this property. As a consequence the tensile strength, percent elongation and percent reduction in area were determined for cast high purity indium. Interest generated by the tensile tests led to a rather comprehensive check of the hardness of indium and an extension of the tensile tests to stress rupture tests, including the plotting of a master rupture curve for indium.

CHAPTER II

REVIEW OF LITERATURE

I. GENERAL INFORMATION

For information concerning the general properties and extraction of indium, the reader is referred to M. T. Ludwick's book, "Indium."[1] It contains a comprehensive survey of the history, occurence, extraction and properties of indium plus a bibliography from 1863 to 1949.

A considerable amount of work has been done with X-ray diffraction to study indium. In 1920, A. W. Hull used a powder method to determine the symmetry and cell dimensions of indium.[2] He specified a face-centered tetragonal unit cell. In that same year, Hull and W. P. Davey applied an indium pattern to their method of plotting indices and axial ratios with fair success.[3] In 1932, F. D. Dwyer and D. P. Mellor performed a more accurate determination of the cell dimensions.[4] Still later in 1933, F. Zintl and S. Neumayr employed

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[1]Maria T. Ludwick, Indium (New York: Indium Corporation of America, 1950) pp. 7-69.

[2]Albert W. Hull, "Arrangement of the Atoms in Some Common Metals," Science, 52: 228, 1920.

[3]Albert W. Hull and W. P. Davey, "Crystal Structure of Indium," Physical Review, 17: 273, 1921.

[4]Francis P. Dwyer and David P. Mellor, "Crystal Structure of Indium," Journal of the Proceedings of the Royal Society of New South Wales, 66: 238-39, 1932.

rotating crystal and Weissenberg methods to obtain accurate cell dimensions.[5] The latest work on cell dimensions of indium was by Graham, Moore and Raynor in 1955 and was concerned with the effect of temperature on lattice spacing.[6] For temperatures from -183°C to +135°C, they found that a_o increased rapidly, c_o increased slightly to a maximum at room temperature and c_o/a_o decreased.

Swanson, Fuyat and Ugrinic in 1954 reported a most complete tabulation of d values, intensities and indices.[7] They also compiled the results of Hull and Hanawalt, Rinn and Freval.[8,9] These values along with the data from the other references are tabulated in Chapter III. They refuted the use of the face-centered cell on the grounds that no space group notation is available and that it can be converted to a body-centered cell by merely rotating 45° about the c axis.

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[5]E. Zintl and S. Neumayr, "Lattice Structure of Indium," Zeitschrift fur Electrocherie, 39:84, 1933.

[6]J. Graham, A. Moore and G. V. Raynor, "The Effect of Temperature on the Lattice Spacings of Indium," Journal of the Institute of Metals, 84:87, 1955.

[7]Howard E. Swanson, Ruth K. Fuyat and G. N. Ugrinic, Standard X-ray Diffraction Powder Patterns, National Bureau of Standards, Circular 539, Vol. 3 (Washington: Government Printing Office, 1954), p. 12.

[8]Hull, loc. cit.

[9]J. D. Hanawalt, H. W. Rinn and L. K. Freval, "Chemical Analysis by X-ray Diffraction," Industrial Engineering Chemistry, Analytical Edition, 10:469, 487, 1938.

The metallography of indium has been investigated by several people in connection with other work on the metal. Carpenter and Tamura, who first observed twinning in indium in the year, 1926, prepared it by pressing between glass plates and etching with a 50% nitric acid solution in water.[10] Carapella and Peretti, who worked on indium alloys in 1949, developed a hand polishing method and used Viella's reagent as an etchant.[11] They also worked out an electropolishing technique using a 1:2 nitric acid and methyl alcohol solution at a current density of 30 amp./dm^2. Goss and Vernon in 1952, used Carapella and Peretti's electrolytic method, but had little success with the above mentioned chemical etchants.[12],[13] They used concentrated hydrochloric acid to which was added potassium chlorate in sufficient amounts to produce chlorine during etching.

II. SINGLE CRYSTAL

Many methods of growing single crystals have been devised. Three of the common ones were investigated by the following persons.

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[10]H.C.H. Carpenter and S. Tamura, "Formation of Twinned Crystals," Royal Society of London, Proceedings, A 113:176-8, 1926.

[11]S. C. Carapella and E. A. Peretti, "Metallography of Indium and Indium-Rich Alloys," Metal Progress, (November, 1949), 666.

[12]A. J. Goss and E. V. Vernon, "The Growth and Orientation of Single Crystals of Indium," Physical Society of London, Proceedings, 65B:906, 1952.

[13]Carapella and Peretti, loc. cit.

In 1953, Bruce Chalmers studied the growth of metal crystals from the melt using a horizontal boat and a moving temperature gradient.[14] He worked with the metals, indium, tin, lead, zinc, aluminum, silver, gold, copper and nickel, with respect to boat material, furnace type, atmosphere, speed of gradient travel, seeding technique and orientation. His recommendations for indium were a graphite boat, tubular wire wound furnace, ordinary air as an atmosphere and a furnace travel of 10 m.m./min. G. P. Bolognesi, in 1955, used a vertical crucible and raised his furnace away from it to grow crystals of tin, lead and aluminum.[15] In 1956, D. N. Kumar used a nearly vertical crucible with a pointed bottom and grew single crystals of silver by merely controlling the cooling rate of an electrical resistance winding around the crucible.[16]

The properties of indium single crystals have been investigated by various people. In 1948, Gwathmey, Leidheiser and Smith studied the influence of crystal plane and surrounding atmosphere on the chemical activities of single crystals of metals.[17] They grew indium

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[14]Bruce Chalmers, "The Preparation of Single Crystals and Bicrystals by the Controlled Solidification of Molten Metals," Canadian Journal of Physics, 31:133, 1953.

[15]G. P. Bolognesi, "The Preparation of Single Crystals of Low-Melting-Point Metals: Description of a New Apparatus and First Results," Revue de Metallurgia, 52: (11) 911, 1955.

[16]D. N. Kumar, "A Method of Growing Single Crystals of Metals," Bulletin, The Institute of Metals, 3: (9), 80, 1956.

[17]Allan T. Gwathmey, Henry Leidheiser and G. Pedro Smith, Influence of Crystal Plane and Surrounding Atmosphere on Chemical Activities of Single Crystals of Metals, National Advisory Committee of Aeronautics, Tech. Note 1460 (Washington: Government Printing Office, 1948) pp. 23-4, 30.

crystals in the shape of a sphere by lowering a glass bulb from a vertical furnace. In 1950, Verhaeghe, Vandermeerasche and LeCompte investigated the susceptibility and magnetic anisotrophy of indium single crystals.[18] The method of growth was not given. A. J. Goss, in 1953, using a horizontal method studied the effect of rates of growth on heat flow and orientation on indium and other metal single crystals.[19] Also in 1953, Vernon and Weintroub measured the thermo-expansion of single crystals of indium and tin with a photoelectric recording dilatometer.[20] The method of growth was not specified. Meissner and Doll, in 1955, checked the resistance and magnetic flux for indium single crystals during the transition to supraconduction with large current flow.[21] They also did not specify a method of growth. And finally in 1958, Winder and Smith determined the single

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[18]J. Verhaeghe, G. Vandermeerache and G. LeCompte, "Susceptibility and Magnetic Anisotrophy of Indium Single Crystals," Physical Review, 80:(4), 758, 1950.

[19]A. J. Goss, "Heat Flow and the Growth of Metal Single Crystals from the Melt," Physical Society of London, Proceedings, 66B:525-32, 1953.

[20]E. V. Vernon and S. Weintroub, "The Measurement of the Thermoexpansion of Single Crystals of Indium and Tin," Physical Society of London, Proceedings, 66B:887-94, 1953.

[21]Walther Meissner and Robert Doll, "Resistance and Magnetic Flux for Indium Single Crystals During the Transition to Supraconduction," Zeitschrift fur Physik, 140:(3), 340-358, 1955.

crystal elastic constants of indium.[22] For their method of growth, they employed a vertical temperature gradient with a 1°C/min. cooling rate.

One of the best methods for the strain-free cutting of single crystals is by etch-cutting. The method was first developed by McGuire and Webber in 1949, in which they used a hack saw like contrivance to pull a fiber glass thread back and forth over the crystal and through an acid bath.[23] In this way a continuous supply of acid was brought into action on a small area of the sample, cutting through a tin crystal, 1 cm. in diameter in about 5 hours. In 1950, Maddin and Asher improved upon McGuire and Webber's design by using a reciprocating drum to drive a plastic thread (Saran), two acid baths, one on each side of the crystal, and a simple goniometer to permit better positioning of the crystal.[24,25] They also used a double thread which enabled them to cut slices from the brass crystals which they were

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[22]D. R. Winder and Charles S. Smith, "Single Crystal Elastic Constants of Indium," Physical Chemistry of Solids, 4: (1/2), 129, 1958.

[23]T. R. McGuire and R. J. Webber, "Etch Cutter," Review of Scientific Instruments, 20:962, 1949.

[24]Robert Maddin and W. R. Asher, "Apparatus for Cutting Metals Strain-Free," Review of Scientific Instruments, 21:882, 1950.

[25]McGuire and Webber, loc. cit.

investigating. Piontelli, Rivolta and Sternheim, in 1955, made still another improvement by incorporating an electrolytic action to speed up the operation.[26] On their modification, the crystal was made the anode and a platinum plate in each bath was the cathode. A current of 30 ma. was used to cut a 20 mm. diameter tin crystal with a 50% nitric acid and water solution. Still later in 1956, Yamamoto and Watanabe made an extensive investigation as to the optimum conditions for the use of the Maddin and Asher modification.[27,28] First they studied the use of various thread materials, the metals, Fe-Cr-Al, Ni-Cr-Fe and copper and the plastics, vinyl chloride and saran. Then, using the plastic threads, which proved to be the best, they cut crystals of tin, zinc, iron, nickel, aluminum, bismuth and copper. They also compared the method with the paraffin technique for tin, zinc and iron. Finally in 1958, Armstrong and Rapp made another change by incorporating burettes to feed the acid on the thread.[29] They achieved times of 12 hours with nitric acid on a 0.75 inch diameter magnesium crystal and several hours with chromic and sulfuric acids on a 0.25 inch diameter silver crystal.

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[26]R. Piontelli, B. Rivolta and G. Sternheim, "Improved Apparatus for Cutting Single Crystals," Review of Scientific Instruments, 26:(12), 1206, 1955.

[27]Mikio Yamamoto and Jiro Watanabe, "Strain-Free Cutting of Metal Single Crystals," Science Reports of the Research Institute, Tohoku University, 8A:230-42, 1956.

[28]Maddin and Asher, loc. cit.

[29]R. W. Armstrong and R. A. Rapp, "Simple Etching Cutter," Review of Scientific Instruments, 29:(5) 433, 1958.

III. RECRYSTALLIZATION TEMPERATURE

Very little mention of the recrystallization temperature of indium has been made. In their work on twinning in 1926, Carpenter and Tamura stated that after annealing at 100°C for two hours, indium was completely recrystallized.[30] Later in the same work, they mentioned that for the most metals the lowest temperature of recrystallization is between 0.35 and 0.45 of the absolute melting point. Gwathmey, Leidheiser and Smith in their paper on chemical activities of single crystals in 1948 stated only that the recrystallization temperature of indium was below room temperature.[31]

A general formula relating the temperature of recrystallization, latent heat of fusion, Debye temperature and the gas constant was proposed by V. L. Schmarts in 1957.[32] It is as follows:

$$L = 3RT_r\left[1 - \frac{3}{8}\frac{\theta}{T_r} + \frac{1}{20}\left(\frac{\theta}{T_r}\right)^2 - \frac{1}{1680}\left(\frac{\theta}{T_r}\right)^4\right]$$

where: L = latent heat of fusion

R = the gas constant

T_r = the recrystallization temperature

θ = the Debye temperature

IV. MECHANICAL PROPERTIES

According to Mellor and Ludwick, W. C. Roberts-Austen made the first determination of the tensile strength of indium back in

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[30] Carpenter and Tamura, loc. cit.

[31] Gwathmey, Leidheiser and Smith, op. cit., p. 30

[32] V. L. Shmarts, "Determination of the Recrystallization Temperature of Metals," Fiz. Metal. i Metalloved., Acad. Nank sssR, 5:184, 1957.

1888.[33,34,35] Roberts-Austen actually did not determine the tensile strength of indium, since he was working on the effect of adding impurities to gold on that metal's tensile strength. He reported a value of 7.99 tons/sq.in. for a gold alloy containing 0.29% indium and this was incorrectly taken as the tensile strength of indium.

In 1900, J. R. Rydberg classified most of the metals on the Moh hardness scale.[36] He assigned a number of 1.2 to indium. Then in 1909, Kurnakow and Zunczuzny, in conjunction with work on the electrical resistance and plastic flow of lead-indium and lead-thallium alloys, made brinell hardness measurements.[37] They obtained a number of 1.19 with a 10 mm. ball and a 50 kg. load.

The next work on mechanical properties had to do with compressibility. Richards and Sameshima in 1920 measured the compressibility of indium at 25°C and from 100 to 510 megabars pressure and found $B = 7 \times 10^{-6}$.[38] In 1928, Richards and White used material of better

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[33]J. W. Mellor, Vol. V of Treatise on Inorganic Chemistry, (16 vols.; New York: Longmans, Green and Co., 1924.)

[34]Ludwick, op. cit., p. 14.

[35]W. Chandler Roberts-Austen, "On Certain Mechanical Properties of Metals," Chemical News, 57:133, 1888.

[36]J. R. Rydberg, "Hardness of Metals on the Moh Hardness Scale," Zeitschrift fur Physikalishe Chemie, 33:356, 1900.

[37]N. Kurnakow and S. Zunczuczy, "Elektrische Leitfahigheit and Fliessdruck isomorpher Gemische des Bleis mit Indium and Thallium," Zeitschrift fur Anorganische Chemie, 64:174, 1909.

[38]Theodore W. Richards and J. Sameshima, "Compressibility of Indium," Journal of the American Chemical Society, 42:49, 1920.

purity and obtained a value of D= 2.55 x 10^{-6} under essentially the same testing conditions.[39]

In 1938, Erich Einecke studied the properties of indium, gallium and thallium.[40] One of his investigations included the scratch hardness of indium as tested on Adolf Martens' machine from which he obtained a table of scratch widths for various loads.[41] He also gave the ratio of hardnesses between gallium, indium and thallium as:

$$H_{Ga} : H_{In} : H_{Tl} = 2.9 : 1.0 : 1.1$$

The National Bureau of Standards, in 1943, made the first general tabulation of the mechanical properties of indium.[42] They listed the following data for indium of 99.9% purity:

Tensile strength	0.43 Kips/sq.in.
Reduction in area	99%
Hardness	Vickers 1.0

The tensile strength was run on a 3/8 inch diameter cast rod, and the hardness test was made with a 200 gm. load for 10 seconds.

Werner Koster, in 1948 studied the temperature dependence of the elastic moduli of pure metals as computed from the harmonic

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[39]Theodore W. Richards and Joseph D. White, "Compressibility of In-Zn alloy, of In and of Other Elements," Journal of the American Chemical Society, 50:3299, 1928.

[40]Erich Einecke, "Gallium, Indium and Thallium," Zeitschrift for Anorganische und Allgemein Chemie, 238:123, 1938.

[41]Adolf Martens, "Ueber Hartebestimmungen," Mitt. kaiserlich. tech. Versuchsanstalt Berlin, 8: (6), 277, 1890.

[42]National Bureau of Standards, Mechanical Properties of Metals, Circular C-447 (Washington: Government Printing Office, 1943), p. 416.

frequency of the metals.[43] At room temperature, 20°C, his value for indium was 1070 kg./mm.^{2} (1.52 x 10^6 psi). The variation with temperature followed a slightly curved path from 1550 kg./mm.^{2} at -180°C to 750 kg./mm.^{2} at the melting point, 156°C.

In 1952, another tabulation of properties was made. This time it was by Jaffee and Weiss in a paper on the commercial uses of indium.[44] They tabulated the following properties:

Hardness	Bhn 0.9
Tensile strength	380 psi.
Elongation in 1 inch	22%
Reduction in area	87%
Compressive strength	310 psi.
Modulus of elasticity	1.57 x 10^6 psi.

No information was given on the purity of the indium or methods of testing.

The last work on the mechanical properties of indium was by C. Rubenstein on the influence of creep on the measured hardness of soft metals.[45] Using indium and lead he proved that the Meyer interpretation of the Brinell hardness test was not applicable to soft metals because of their tendency to creep during test.[46]

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[43]Werner Koster, "Die Temperaturabhangigkeit des Elastizitatsmoduls reiner Metalle." Zeitschrift fur Metallkunde, 39:3, 7, 1948.

[44]R. I. Jaffee and S. Marguerite Weiss, "Indium Alloys Finding Important Uses," Materials and Methods, 36: (September, 1952), 115.

[45]C. Rubenstein, "The Influence of Creep on the Measured Hardness of Soft Metals," Physical Society of London, Proceedings, 67B: 563, 1954.

[46]Eugen Meyer, "Untersuchungen uber Harteprufung und Harte," Zritschrift fur Vereinsdt deutsch Ingenieur, 52:(17), 645-54, 1908.

No previous work has been done on the stress rupture properties of indium. The procedure for stress rupture tests was developed in 1938 by White, Clark and Wilson for steels at high temperatures.[47] Then in 1952, Larson and Miller employed the parameter, T(C + log t), to plot stress rupture data in the form of a master rupture curve.[48]

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[47]A. E. White, C. L. Clark and R. L. Wilson, "The Rupture Strength of Steels at Elevated Temperatures," Transactions of the American Society of Metals, 26:54-56, 1938.

[48]F. R. Larson and James Miller, "A Time-Temperature Relationship for Rupture and Creep Stresses," Transactions of the American Society of Mechanical Engineers, 74:769, 1952.

CHAPTER III

GENERAL INFORMATION

I. SPECTROGRAPHIC ANALYSIS

A certain amount of general information seemed to be necessary to carry out properly this investigation. The first of this information was a spectrographic analysis of the indium to determine the nature of the impurities present and the pick-up of impurities during the course of the investigation.

An Applied Research Laboratories' grating spectrograph in the Metallurgy Department of the Missouri School of Mines was used for the analysis. Two different spectra were taken of the original indium shot as obtained from the Indium Corporation of America. Another spectrum was made toward the end of the investigation of some of the indium that had been used again and again during the research. An interpretation of these spectra is presented by Table I. The results were, with use the indium has picked up small amounts of lead and tin and lost aluminum. The amounts of lead and tin picked up could easily have come from carry over on equipment since these two metals were used in various instances to check the apparatus used in the study. The loss of aluminum was probably due to selective oxidation during the many meltings which were performed, most of it probably being concentrated in the oxide films formed during the melting and casting operations.

TABLE I

RESULTS OF THE SPECTRUM
ANALYSIS OF INDIUM

	Spectra from indium shot		Spectrum from used indium
Spectra No.	1	2	1
Major impurities	Fe	Fe	Pb
	Al	Al	Fe
Trace Impurities	Pb	Cu	Sn
	Mn	Mg	Cu
		Mn	Mg
			Mn

II. METALLOGRAPHY

A knowledge of the metallography of indium was essential to the evaluation and interpretation of experimental results. The methods of Carapella and Peretti were tried with little success.[49] Their polishing procedures were developed for indium alloys and were not suitable for the soft pure metal. Their etchant was also found to be lacking in that it showed no grain orientation or contrast. The following three procedures were developed:

Procedure one

a. Cut off sample with pocket knife
b. Grind on 600 grit wet paper
c. Intermediate polish with 6-10 micron diamond compound on Metcloth
d. Final polish with Linde B on Selvyt
e. Etch with aqua regia
f. Wash with water and dry

Procedure two

a. Cut off sample with etch-cutter (The etch-cutter is described in detail in Chapter IV)
b., c., d., e. and f. are the same as in procedure one

Procedure three

a. Roll sample (at least 50% reduction)

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[49]Carapella and Peretti, loc. cit.

b. Etch with aqua regia

c. Wash with water and dry

The first procedure is satisfactory for ordinary preparation for the general observation of the microstructure. The final polish does not result in a shiny finish; its only purpose is to obtain a smooth surface. The etchant first removes the dull surface left by the final polish, and then reveals the structure. Figure 1 shows a typical microstructure of indium prepared in this way.

Procedure two is used if one wishes to examine as cast or other microstructures in an undistrubed condition. Procedure one of course cold works the specimen surface and the resulting microstructures are, therefore, of recrystallized material. Figure 2 is an "as cast" microstructure of indium prepared by procedure two.

Procedure three could possibly be employed to examine the rolled structure or as a fast method for study of the recrystallized structure. Figure 3 is a typical recrystallized structure prepared by this method with rolling to an 80% reduction.

In all cases, the aqua regia etch is used at room temperature with immersion of the specimen. The time for etching is approximately one minute; the best technique, however, is to etch to the desired structure. If the specimen becomes overetched, it can be brightened by immersion in concentrated nitric acid, and then re-etched in aqua regia. This does result in some etchpits and etching relief however. The concentrated nitric acid leaves the grain boundaries, but does not show the twins or any grain contrast.

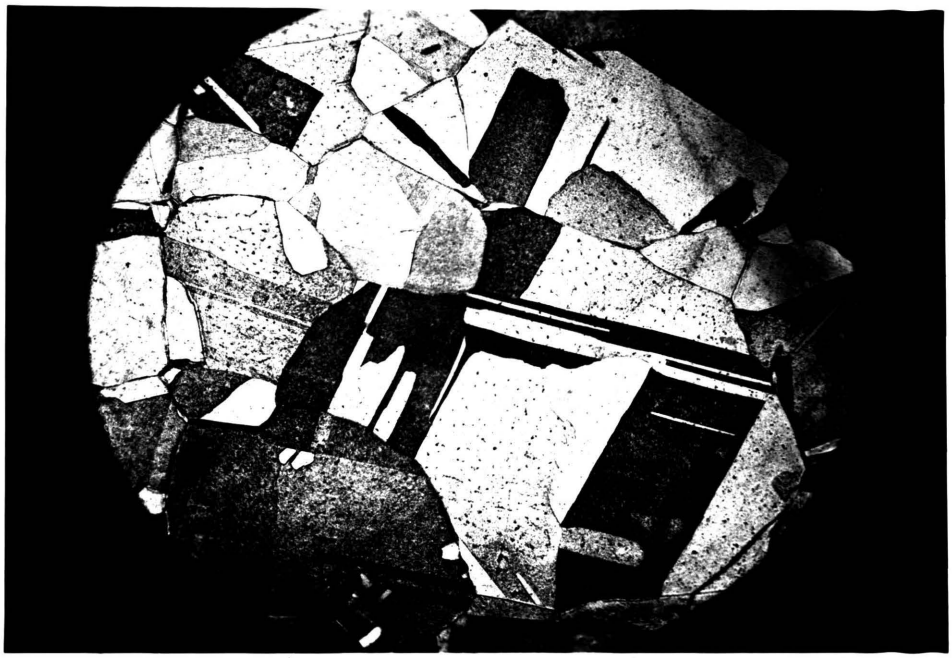

Figure 1. Microstructure of indium, prepared by procedure one, 25X, aqua regia etch.

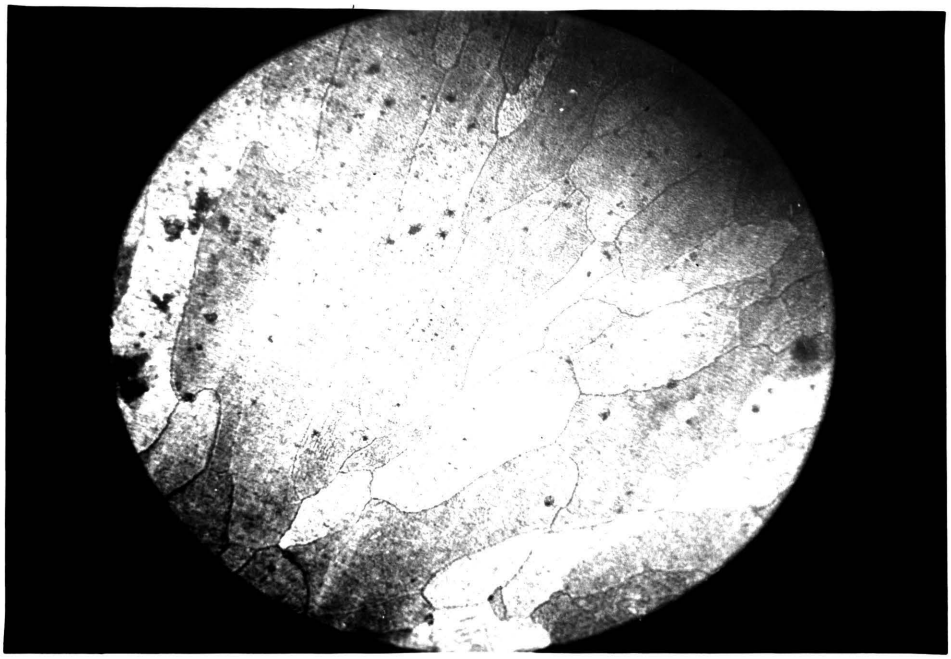

Figure 2. Microstructure of as cast indium, prepared by procedure two, 25X, aqua regia etch.

Figure 3. Microstructure of rolled indium, prepared by procedure three, 100X, aqua regia etch.

Washing with alcohol is to be avoided as it tends to dull the etch. For this reason ordinary tap water is used for washing and the specimen is dried in air.

III. X-RAY DIFFRACTION

The need for X-ray diffraction data for indium was anticipated for the work on recrystallization. A sample was prepared by compressing a one inch long, one-half inch diameter cast indium specimen, of the type used later in the hardness tests, to a one-fourth inch height and a one inch diameter. The specimen was then etched in aqua regia to remove the flowed metal on the surface and reveal the grain size. The grain size was estimated to be an average grain diameter of 0.200 mm.

First of all a diffraction pattern was run on the Norelco Geiger-tube Spectrometer in the Ceramics Department of the Missouri School of Mines, using nickel-filtered, copper radiation. The data obtained are tabulated in Table II. The d values in the table were calculated with Bragg's Law, $n\lambda = 2D \sin\theta$ and λ for Cu $K\alpha_1$ = 1.5374A.[50] A check of the literature revealed an apparent discrepancy in the Miller indices assigned to the crystal planes by the various investigators.[51,52,53,54]

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[50]Charles D. Hodgman (ed.), Handbook of Chemistry and Physics (37th edition; Cleveland: Chemical Rubber Publishing Co., 1955), p. 2417.

[51]Hull, loc. cit.

[52]Dwyer and Mellor, op. cit., p. 238

[53]Zintl and Neumayr, loc. cit.

[54]Swanson, Fuyat and Ugrinic, loc. cit.

TABLE II

DATA FROM FIRST X-RAY PATTERN

2θ in degrees	d in A.	Relative Intensity
33.50	2.670	100
36.70	2.440	17
39.50	2.270	16
54.70	1.670	28
56.75	1.620	3
63.35	1.465	9
67.20	1.390	9
69.20	1.355	13
89.85	1.090	5

Therefore, it seemed desirable to obtain a more accurate and extensive pattern. Consequently, another pattern was run on the newer model Norelco Geiger-tube Spectrometer in the Metallurgy Department and the d values calculated as for the first pattern. The data for this pattern are presented in Table III along with the Miller indices for the diffracting planes as calculated with the following tetragonal indexing formula:

$$d = a_o / \sqrt{h^2+k^2+(l/c)^2}$$

where $a_o = 4.583 \pm 0.002$ and $c = c_o/a_o = 1.077 \pm 0.001$[55]

The indices were also checked using the $\sin^2\theta$ method as demonstrated by B. D. Cullity, which employed the quadratic formula:

$$\sin^2\theta = A(h^2+k^2) + Cl^2$$

where $A = \lambda^2/4a_o^2$ and $C = \lambda^2/4C_o^2$.[56] The constants A and C were evaluated as 0.02803 and 0.02430 respectively. From which: $a_o=4.652$ and $c_o=4.932$.

Table IV is a tabulation of all known X-ray data. The Miller indices in the last column are those assigned by Swanson, Fuyat and Ugrinic.[57] These indices are in apparent disagreement with those of all the other investigators and the data of this investigator. The reason for this disagreement is a difference in the interpretation of

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[55]Zintl and Neumayr, loc. cit.

[56]B. D. Cullity, Elements of X-Ray Diffraction (Reading, Mass.: Addison-Wesley Publishing Company, 1956), pp. 312-313.

[57]Swanson, Fuyat and Ugrinic, loc. cit.

TABLE XII

DATA FROM SECOND X-RAY PATTERN

2θ in degrees	d in A.	Relative Intensity	hkl	d(calc.) in A.
32.90	2.715	100	111	2.709
36.67	2.470	11	002	2.469
39.13	2.295	18	200	2.291
54.43	1.681	24	202	1.679
56.50	1.624	4	220	1.619
63.17	1.468	6	113	1.468
67.03	1.392	5	311	1.392
69.07	1.356	15	222	1.355
77.37	1.230	1	004	1.235
84.47	1.144	1	400	1.146
89.87	1.088	6	313	1.088
93.27	1.057	2	331	1.057
95.23	1.041	1	402	1.039
96.97	1.027	3	420	1.025
102.90	0.983	2	224	0.982
108.40	0.950	2	422	0.947
116.43	0.904	4	333	0.903
120.40	0.886	1	511	0.885
132.20	0.841	1	404	0.839
140.63	0.816	1	315	0.817

TABLE IV

ALL OTHER KNOWN X-RAY DATA

hkl	Hull d in A.	Hull Rel. Int.	Dwyer & Mellor d in A.	Dwyer & Mellor Rel. Int.	Zintl & Neumayr d in A.	Zintl & Neumayr Rel. Int.	Hanawalt, Rinn & Frevel d in A.	Hanawalt, Rinn & Frevel Rel. Int.	Swanson, Fuyat & Ugrinic d in A.	Swanson, Fuyat & Ugrinic Rel. Int.	hkl
111	2.700	20	2.714	10	2.709		2.730	100	2.715	100	101
002	2.420	0.5			2.467		2.460	25	2.471	21	002
200	2.290	5	2.295	2	2.291		2.290	40	2.298	36	110
202	1.675	2	1.684	3	1.680		1.680	30	1.683	24	112
220	1.617	0.5	1.622	0.5			1.620	15	1.625	12	200
113	1.450	1	1.470	1.5	1.467		1.465	20	1.470	16	103
311	1.392	2	1.392	5.0	1.392		1.398	30	1.395	23	211
222	1.348	2	1.356	1	1.355		1.358	15	1.359	11	202
									1.2363	3	004
400	1.150	0.25					1.146	2	1.1493	5	220
313	1.080	1			1.088		1.090	10	1.0904	12	213
331					1.056		1.057	2	1.0587	4	301
402					1.038		1.042	2	1.0425	5	222
420					1.025		1.027	2	1.0282	8	310
224					0.982		0.982	2	0.9845	1	204
422					0.947		0.950	6	0.9495	3	312
333							0.907	2	0.9056	2	303
511							0.890	2	0.8874	4	321
Radiation	Mo		Cu		Cu		Mo		Cu		
a_o	4.58		4.588 + 0.002		4.583 + 0.002						
c_o	4.86		4.946 ∓ 0.002		4.936 ∓ 0.002						
c_o/a_o	1.06		1.078 ∓ 0.002		1.077 ∓ 0.001						
density	7.42		7.28		7.308						

the unit cell of indium. Swanson, Fuyat and Ugrinic, by a 45° rotation about the c axis, obtained a body-centered-tetragonal cell with an a_o of 3.2517A., a C_o of 4.959A. and a space group of $D_4^{17}h$ / I4/mmm.[58] The above interpretation is justified by the absence of the face-centered-tetragonal lattice in space group notation.

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[58]Ibid

CHAPTER IV

I. GROWING SINGLE CRYSTALS OF INDIUM

The growing of single crystals of indium was the initial part of this investigation. For convenience a horizontal tube-traveling furnace method was used, since a unit of this type was already under construction in the Metallurgy Department. For details of construction and photographs of the equipment, see Appendix A.

The essential operating features of the unit are:

a. an independently supported furnace tube.

b. a traveling furnace with a heating zone 3 1/2 inches long and a variable speed of travel along the tube.

Thirty indium and two tin crystal growing trials were made, producing five indium single crystals. Macro-etching with concentrated nitric acid was used as a preliminary test of singleness for the indium crystals. Certain optimum conditions for the growing of indium single crystals were learned during these attempts. First of all it was necessary to precast the metal in the boat to be used in the attempt to prevent the separation of various parts of the sample due to surface tension of the oxide film on the surface of the individual parts. This also provided an opportunity to control the shape of the crystal.

A second condition to be altered was the length of the furnace zone and the size of the tube. The first trials were made in a 3 inch diameter tube with a heating zone 12 inches long. Eventually it was

reduced to a 1 inch diameter tube with a heating zone 3 1/2 inches long which resulted in more concentration of the heat and a sharper temperature gradient when the zone was moved.

The shape of the boat was also of importance. Figure 4 shows the shape of the boat which was made of graphite. Notice the taper at one end. This was the end which froze first and allowed only one crystal to grow along the length of the boat. It was necessary, when the sample was cast in the boat, before attempting to grow a crystal, that the end of the sample be drawn into the tapered end of the boat.

Another variable was the speed of furnace travel. It was varied from 0.9 to 4 inches per hour. The four inch per hour speed worked the best.

The last important variables were the amount of superheating and the soaking time at the superheating temperature. The optimum seemed to be about 200°F above the melting point for a period of about three hours, which allowed adequate time for complete homogenization of the sample.

Figure 5 shows the effect of time and distance of travel on the temperature at the freezing end of the boat. The curves indicate that the rates of temperature drop at the freezing point are rather high, 340°F per hour and 70°F per inch of travel.

In conclusion, the optimum conditions for growing indium single crystals in a horizontal tube-moving zone furnace of this type are:

a. Pre-casting of the metal in the boat

b. A 3 1/2 inch long and 3 inch diameter heating zone around a 1 inch furnace tube

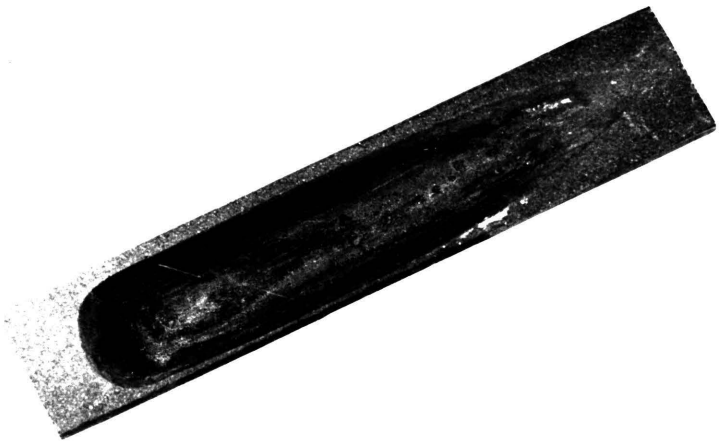

Figure 4. Photograph of graphite crystal boat.

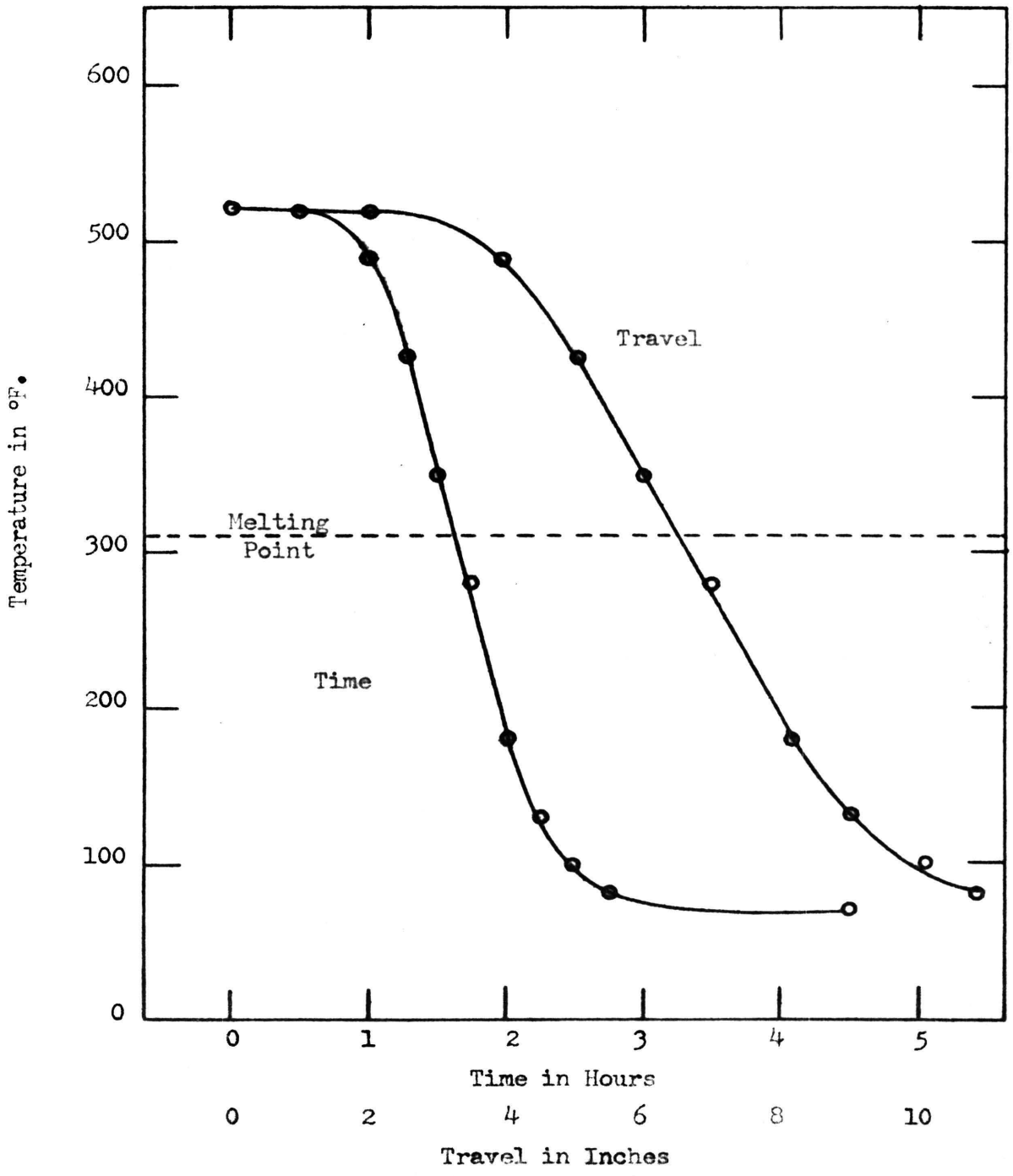

Figure 5. Effect of time and distance of travel on temperature of the crystal boat.

c. A tapered end on the cooler end of the boat

d. A travel of the heated zone of about 4 inches per hour

e. A superheat of 200°F above the melting point for 3 hours

II. SECTIONING OF INDIUM SINGLE CRYSTALS

Sectioning of indium single crystals became a major problem since the metal recrystallized below room temperature and most ordinary cutting methods involved cold work. A method was needed which did not strain or cold work the crystal to prevent recrystallization. A check of the literature yielded a method called "etch-cutting." The basic principle of this method was the application of a small amount of etchant to the surface of the crystal in a definite constricted area which was accomplished by drawing a plastic thread back and forth over the crystal after passing it through an acid bath. To incorporate this method, it was necessary to construct an etch cutter. The sketches of Yamamoto and Watanabe were used as a pattern for designing the apparatus.[59] The details of construction of the etch-cutter are presented in Appendix B.

After construction of the cutter, a suitable procedure for cutting indium crystals had to be developed. First of all a piece of tin was cut using a solution of 1:1 nitric acid and water at a speed of 10 cycles per minute in a time of 3 hours. This compared favorably with previous work by other investigators and proved the soundness of the

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[59] Yamamoto and Watanabe, op. cit., p. 233.

present design.[60],[61]

The next step was to try the etch-cutter on indium crystals. First various etching solutions were tried. Concentrated and 1:1 water solutions of hydrochloric acid, aqua regia, sulfuric acid and nitric acid with a thread travel of 10 cycles per minute were attempted. Then the thread travel was varied with concentrated nitric acid as the etchant from 10 to 22 cycles per minute. No satisfactory cuts were made. The times were too long; the higher speeds caused excessive thread wear; and many of the acids fumed a great deal.

The solution to the problem was found by employing the ideas of Piontelli, Rivolta and Sternheim, who suggested the use of an electric current to speed up the etching process.[62] This was accomplished by making the crystal the anode and a platinum plate in each bath of etchant the cathode. First a voltage of 9 V.D.C. was tried, but because of the high internal resistance of the cell this did not supply enough current to be of help. Next a voltage of 230 V.D.C. was used which gave a plating current of about 6-10 m.a. The crystal was cut in approximately three hours with a solution of 1:1 nitric acid and water and a thread travel of 10 cycles per minute. The method was subsequently used numerous times through the investigation with times running between 1.5 and 3 hours for specimens up to 3/8 inch in diameter.

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[60] McGuire and Webber, loc. cit.

[61] Yamamoto and Watanabe, op. cit, p. 237.

[62] Piontelli, Rivolta and Sternheim, loc. cit.

The surface of the cut was not always smooth, but in all cases was strain free. This can be readily verified by observing the photomicrograph in Figure 2 which shows an "as cast" structure which was cut by the etch cutter. The presence of the columnar grains and the absence of twinning conclusively show that no recrystallization has occurred which in turn indicates the absence of strain.

CHAPTER V

RECRYSTALLIZATION TEMPERATURE OF INDIUM

I. GENERAL CONSIDERATIONS

As mentioned before in the literature review, Carpenter and Tamura stated the relation that the lowest temperature of recrystallization for most metals is between 0.35 and 0.45 of the absolute melting point.[63] Using a value of 155°C (428°K.) for the melting point of indium, the relation would place the lowest recrystallization temperature for indium between -123°C (150°K.) and -80°C (193°K.)[64]

Another relationship was proposed by V. L. Shmarts relating the recrystallization temperature to the latent heat of fusion, the gas constant and the Debye characteristic temperature.[65] This equation states:

$$L = 3RT_r \left[1 - 3/8 \frac{\theta}{T_r} + \frac{1}{20} \left(\frac{\theta}{T_r}\right)^2 - \frac{1}{1680} \left(\frac{\theta}{T_r}\right)^4\right]$$

where:

L = the latent heat of fusion

R = the gas constant

T_r = the recrystallization temperature

θ = the Debye characteristic temperature

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[63] Carpenter and Tamura, op. cit., p. 178

[64] Ludwick, op. cit., p. 14.

[65] Shmarts, loc. cit.

Using L = 0.781 cal./mole, R = 1.9865 cal./°C/mole and θ = 100°K., the recrystallization temperature of indium is computed to be approximately -107°C (166°K.).[66,67,68]

Although these two relationships are in good agreement, their value is questionable. Both of them gave rather erratic results when checked for other metals with low recrystallization temperatures such as lead, cadmium and zinc.

II. ELECTRICAL RESISTANCE

It was suspected that the electrical resistance of a cold worked wire would decrease when it was annealed. Copper wires were used as a check. The resistance was measured with a wheatstone bridge circuit as shown in Figure 6., where R_1 is a slide wire resistor, R_2 is a copper wire annealed for two hours at 1000°F., R_3 is a cold worked copper wire, R_4 is a calibrated variable resistor, G is a galvanometer and B is a 3 volt D.C. power source. After the bridge circuit was balanced using the slide wire, R_1, the resistance on R_4 was noted and the cold worked wire, R_3, was annealed for a time of one hour at increasing temperatures from 600°F to 1100°F. Between the 800° and 900° anneals, the resistance dropped one ohm as indicated by the change in

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[66]Willy Oelsen, Olaf Oelsen and Dieter Thiel, "Precision Determination of Heat of Fusion," Zeitschrift fur Metalkunde, 46:560, 1955.

[67]Hodgman, op. cit., p. 2895.

[68]Frederick Seitz, The Physics of Metals (New York: McGraw-Hill Book Company, 1943), p. 59.

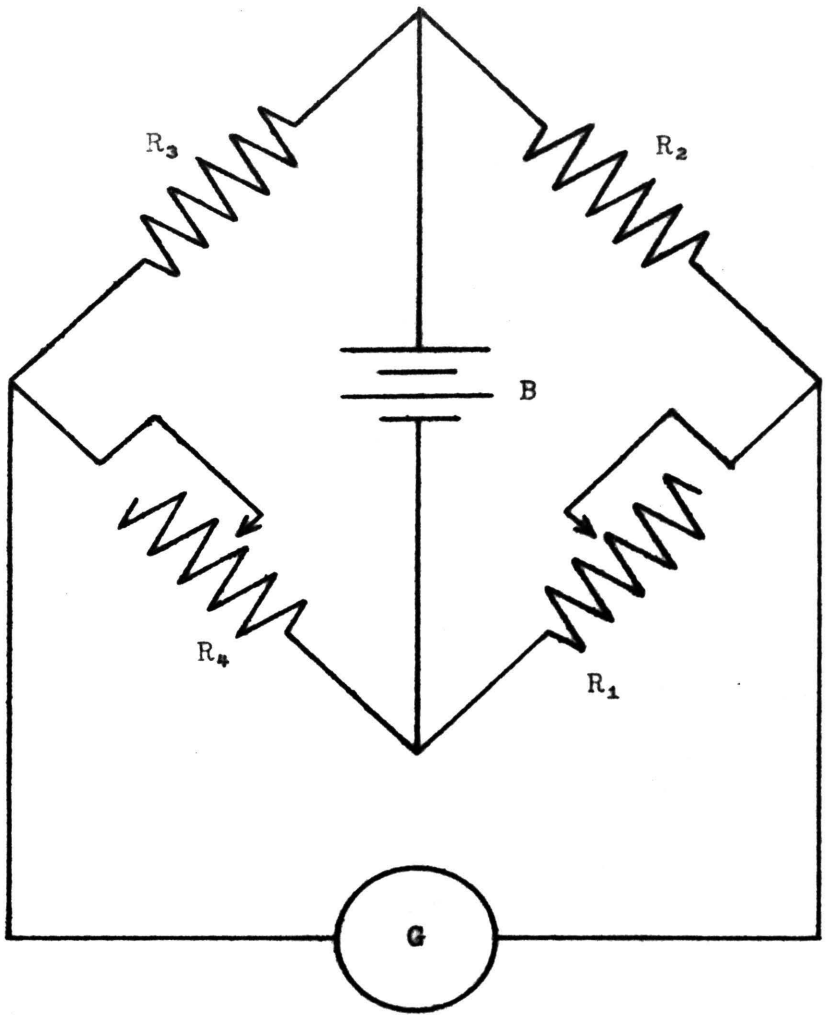

Figure 6. Wheatstone bridge circuit used for resistance measurements.

R_4 necessary to balance the bridge. A repeat of the experiment was made in which the cold worked wire was annealed continuously in a tube furnace. By this method the connections remained unbroken throughout the test which eliminated errors which might have been introduced by poor contacts, and the annealed wire was heated along with the cold worked one to compensate for temperature change effects. The tube furnace temperature was increased in increments of 100°F an hour from 500° to 1100°F. The resistance of R_3 decreased one ohm between 900° and 1000°F.

The next step in the procedure was to repeat the experiment for indium. Indium wires of about 0.10 inch in diameter were prepared by swaging, since the indium was too soft to draw easily. A dry ice-acetone bath was used to obtain a -79°C temperature, and the temperature was measured with a copper-constantan thermocouple and a Leeds and Northrup precision potentiometer.[69] The cold worked wire was cold

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[69]Calibration of the copper-constantan thermocouple

Temperature in °C.	Standard	Thermocouple M.V.	Temp. in °C.
-78.5	Dry ice-Acetone	-2.703	-78.075
-38.87	Hg (M.P.) cooling	-1.425	-38.834
	heating	-1.407	-38.234
0.5	Hg thermometer	0.100	2.570
27.0	Hg thermometer	1.103	27.827
101.0	Hg thermometer	4.320	101.000

worked by bending while it was in the low temperature bath. The annealing was to have been accomplished by allowing the bath to rise to room temperature. The experiment was abandoned, however, because the dry ice and acetone bath was too good an electrolyte.

Some value was salvaged from the experiment, however, by interpreting some data obtained by C. A. Swenson.[7] In conjunction with his work on the properties of indium and thallium at low temperatures, he measured the resistivity of indium from 4.2° to 272.2°K. He observed a change in slope of his curve of electrical resistance versus temperature at 210°K. (-63°C). Two runs on wires from different sources and of 0.015 and 0.020 inches in diameter were made with identical results. A possible explanation is that the wires were slightly cold worked at some time during the period when they were below the recrystallization temperature and recrystallized on heating to cause a change in the resistivity.

III. THERMO ELECTROMOTIVE FORCE

Another phenomena of recrystallization is the change in thermo electromotive force of a cold worked wire upon recrystallization. This property was checked using a copper-constantan couple. First a couple, made up of a cold worked copper wire and a constantan wire, was heated to 1200°F, and the e.m.f. in millivolts was plotted against temperature in °F. The couple was then allowed to remain at 1200°F for two hours

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[7] C. A. Swenson, "Properties of Indium and Thallium at Low Temperatures," Physical Review, 100:1613, 1955.

which thoroughly annealed the copper wire. Then the same couple, after cooling, was heated to 1200°F again, and the e.m.f. was plotted against temperature as before. The two curves coincided after 750°F and showed slight deviation below this temperature which proves the validity of the experiment.

The next step again was to attempt the same experiment with indium. First a suitable couple had to be found between indium and some other metal. Copper was tried, but the resulting e.m.f. was negligible. This result indicated that probably indium was a positive metal like copper and that an indium-constantan couple would work. Consequently, this combination was tried and produced an e.m.f. of 3.933 m.v. at 92°C as shown on the indium-constantan thermocouple calibration curve in Figure 7.

The procedure for the experiment with the indium-constantan couple was essentially the same as with the copper-constantan except that the indium was worked at -70°C and allowed to heat to 0°C. The e.m.f. was plotted against temperature as before. Table V shows the data and Figure 8 shows the curves. The curves coincided at approximately -50°C, which can be assumed to be the recrystallization temperature in this case.

IV. HARDNESS

The effect of recrystallization on hardness is a very much investigated phenomena. The general result is a decrease in hardness at the beginning of recrystallization. To obtain hardness data for

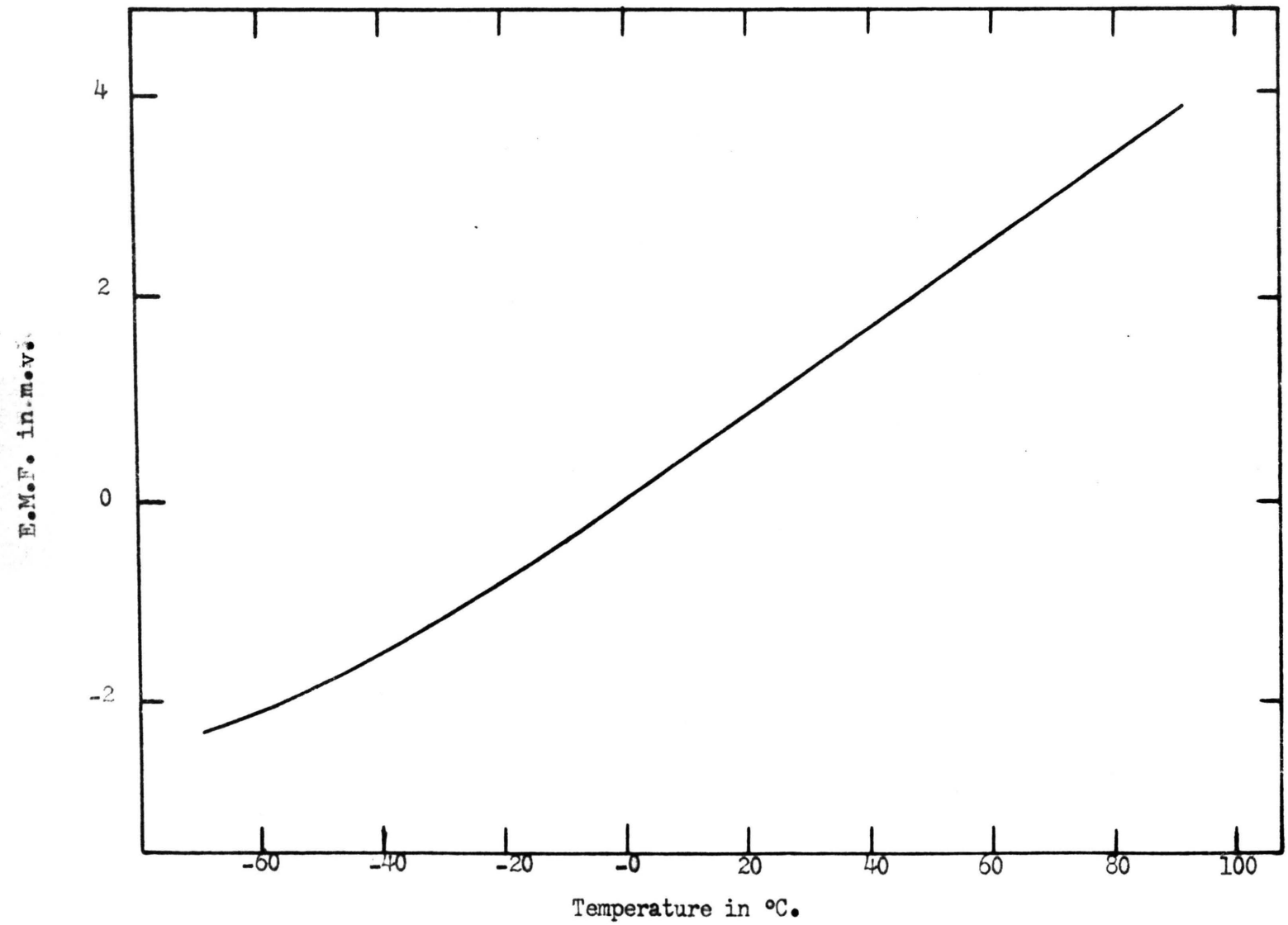

Figure 7. Indium-constantan thermocouple calibration curve.

TABLE V

DATA ON INDIUM-CONSTANTAN THERMOCOUPLE

Calibration		Recrystallization Experiment			
		Cold Worked		Annealed	
Temp. in °C	E.M.F. in m.v.	Temp. in °C	E.M.F. in m.v.	Temp. in °C	E.M.F. in m.v.
28	1.110				
40	1.805	61	2.213	68.5	2.311
		58	2.099	65	2.263
50	2.205	55	2.018	59	2.080
		53	1.913	56	2.014
60	2.625	49	1.785	53	1.913
		47	1.704	49	1.778
70	3.000	44	1.600	46	1.671
		41	1.510	43	1.582
80	3.421	38	1.399	41	1.477
		35	1.291	37.5	1.374
92	3.933	33.5	1.200	35	1.262
		30.5	1.093	32	1.169
		27	1.005	29	1.069
		25	0.910	26	0.963
		22	0.802	23	0.870
		19	0.707	20	0.764
		16	0.603	17	0.649
		13	0.499	14.5	0.549
		10	0.389	12	0.450
		8	0.294	9	0.348
		5	0.204	7	0.249
		3	0.100	4	0.152
		0	0.000	1	0.044
				0	0.000

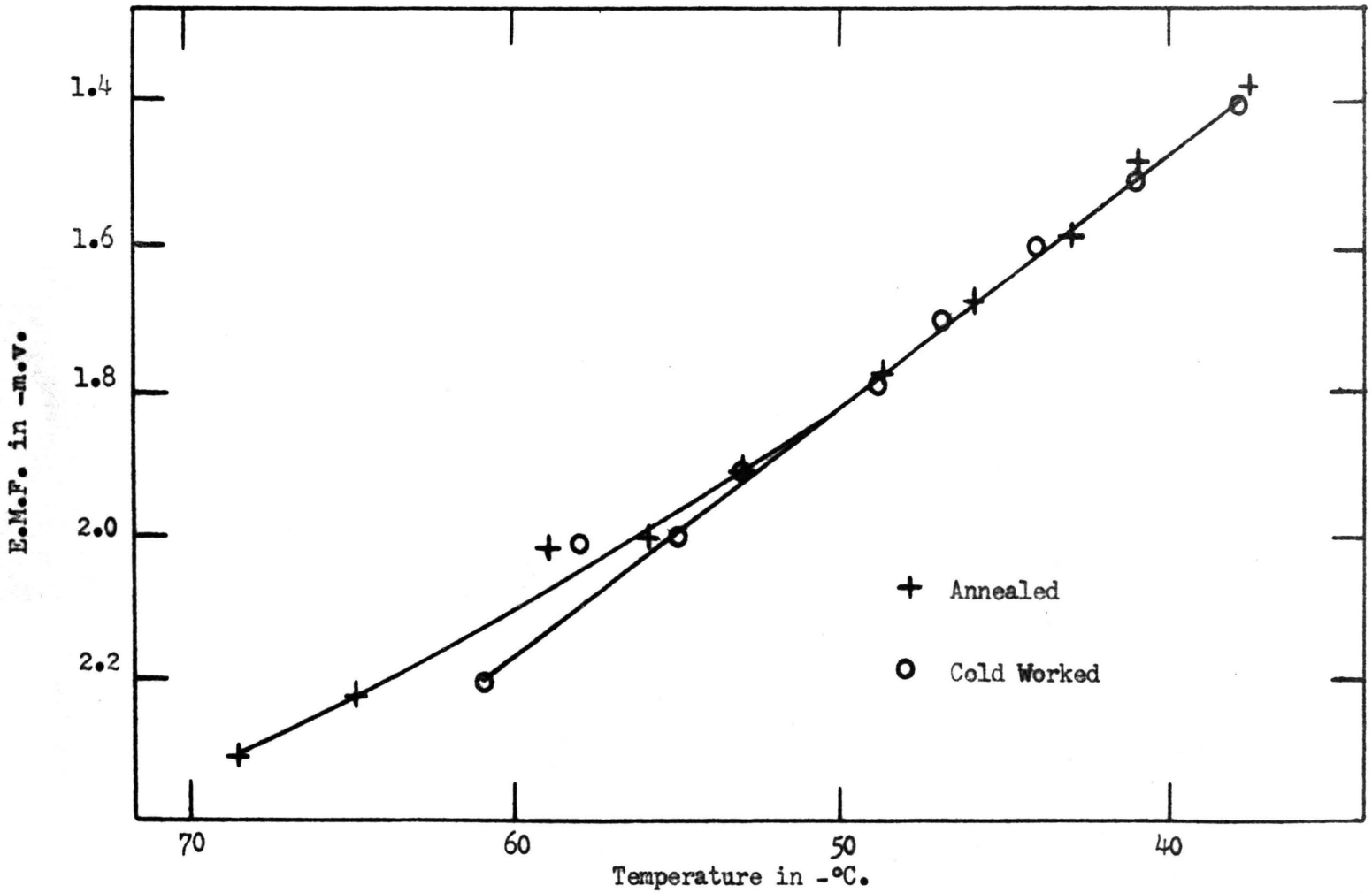

Figure 8. Effect of recrystallization on the e.m.f. on anindium-constantan thermocouple.

indium, the following procedure was used: specimens were cast in graphite molds, cold worked in compression (50%) at -70°C and annealed for one hour at various temperatures from -70° to 30°C. Then after measuring the hardness, a plot was made of the hardness versus annealing temperature.

The specimens were cast 1 inch long and 1/2 inch in diameter and compressed at -70°C to 1/2 inch long. The -70°C temperature was maintained by immersing the entire compressing fixture in a bath of dry ice and acetone and compressing it in a specimen mounting press. The annealing was accomplished in another dry ice and acetone bath which was held at the temperature desired. The temperatures were measured with the copper-constantan thermocouple and potentiometer used in the resistance tests, and were held to $\pm$ 1°C by the careful addition of dry ice. The hardness was measured by dropping a brass ball, weighing 17.6 gm., through a distance of 48 cm. and measuring with a Brinell microscope. A comparison of this method to standard Brinell tests at room temperature gave the following relationship for an approximate computation of Brinell numbers:

$$Bhn = \frac{3.023}{D}$$

where: D is the diameter of the impression for this test in mm. Its validity at other temperatures was not checked.

A total of thirty-two tests were made at annealing temperatures from -70° to 30°C with three specimens in each test. Figure 9 is a photograph showing three specimens, as cast, as compressed and as indented. Table VI is a summary of the results and Figure 10 is a plot of that data. Two curves were plotted; the first is an average of

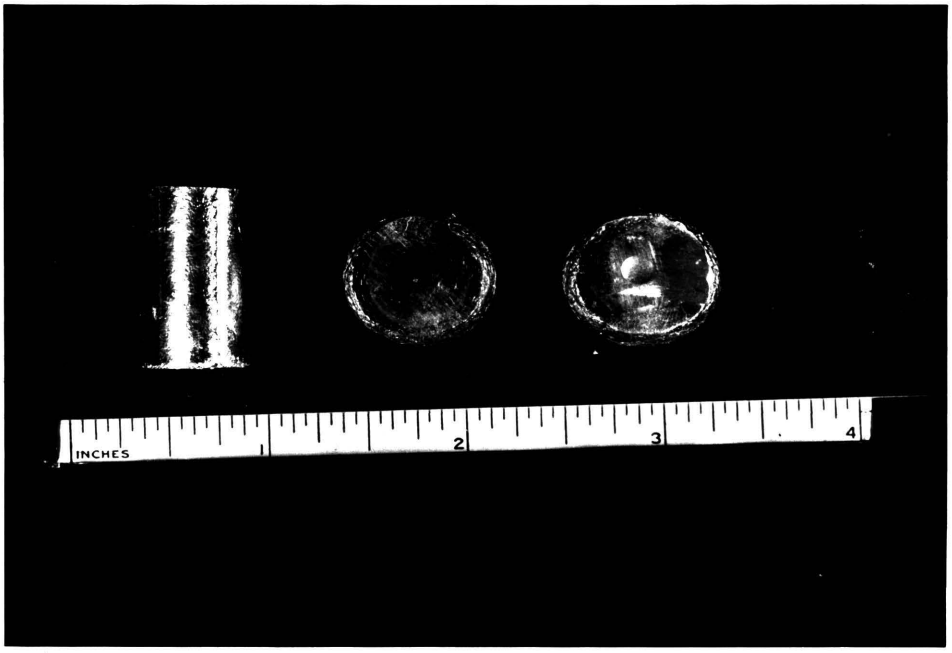

Figure 9. Three hardness specimens, as cast, as compressed and as indented.

TABLE VI

HARDNESS VERSUS ANNEALING TEMPERATURE

Temp.	Diam. of Impression in mm. Adjusted Average	Average of 20 best tests
-69.5	3.65	3.85
-65.0	3.94	3.93
-60.0	3.92	3.97
-55.0	4.05	4.05
-50.0	3.99	4.00
-45.0	4.15	4.15
-40.0	4.15	4.13
-35.0	4.17	4.17
-30.0	4.11	4.18
-25.0	4.07	4.06
-20.0	4.17	4.19
-15.0	4.12	4.12
-10.0	4.18	4.22
-5.0	4.23	4.22
0.0	4.15	--
5.0	4.25	4.23
15.0	4.25	4.25
28.5	4.20	4.23

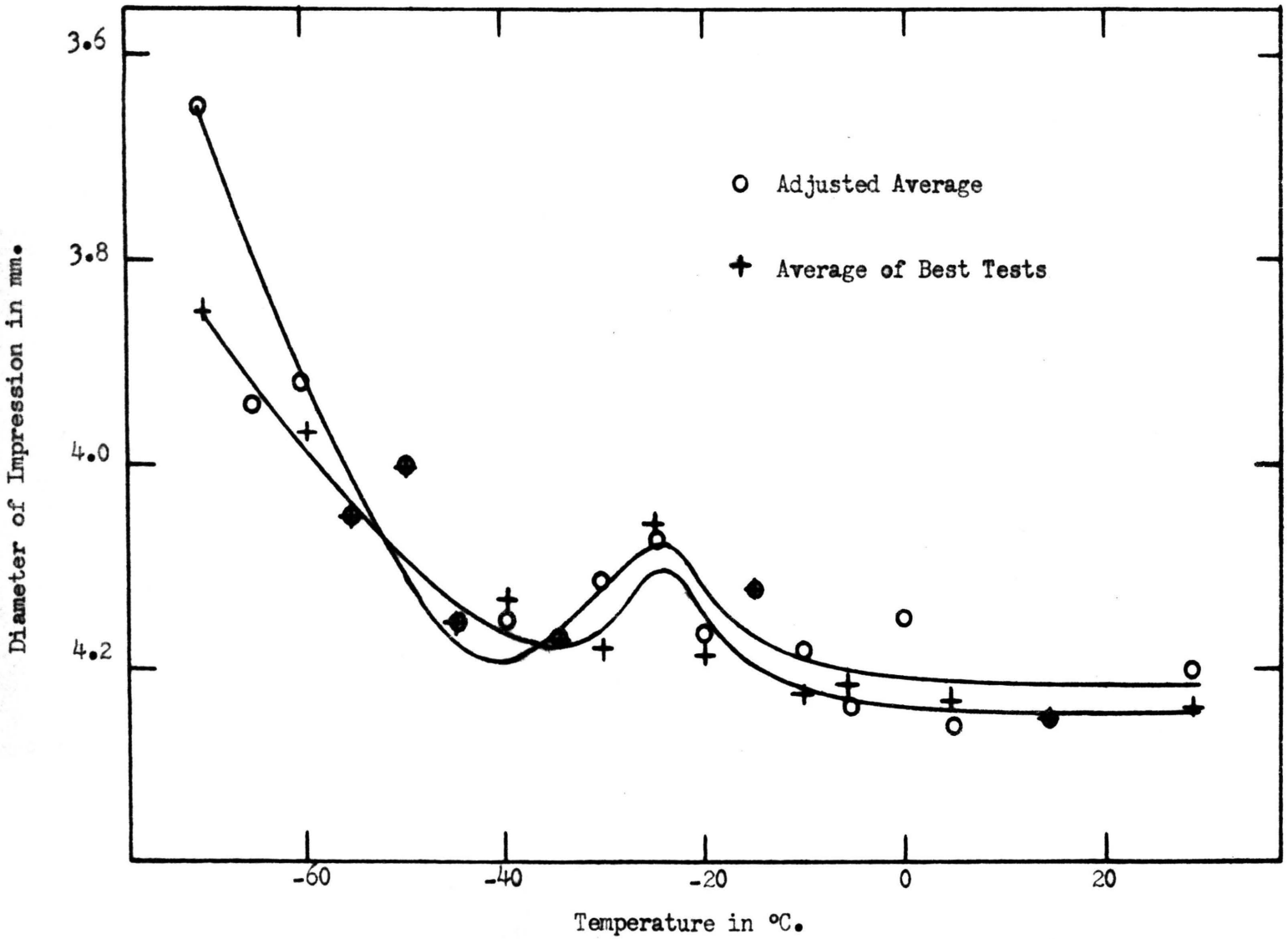

Figure 10. Effect of recrystallization on the hardness of indium.

twenty tests which were considered to be more accurate at the time of performance and the second is an adjusted average of all tests taken after throwing out all values which deviated more than 2.91 times the probable error (the probable error was computed by the formula, $p = \pm 0.6745 \sqrt{\frac{\Sigma (d)^2}{n-1}}$ where p is the probable error, d is the deviation and n is the number of tests).

Two significant things were evident from this plot. First, for this amount of cold work, the temperature at which recrystallization started was below -70°C with the temperature for completion at -35°C. The second was the appearance of a slight rise in hardness just after recrystallization was complete; the cause of which is difficult to explain.

V. BENDING DEFLECTION

The load required to bend a beam at various temperatures should be an indication of recrystallization. Below the recrystallization temperature, the beam should require a greater load to bend it a definite amount because of the resistance to deformation caused by the cold working of the beam. On the other hand above the recrystallization temperature the beam should bend freely with no cold work effect to resist it.

To test this effect a simple testing device was constructed in which a small beam of indium could be bent between three inch centers to a definite deflection. Figure 11 is a photograph of the apparatus as used for the test. Beams of indium 4 inches long and 1/4 inch square were cast in a graphite mold (Figure 12). The beam and centers were immersed in a dry ice and acetone bath at the various testing

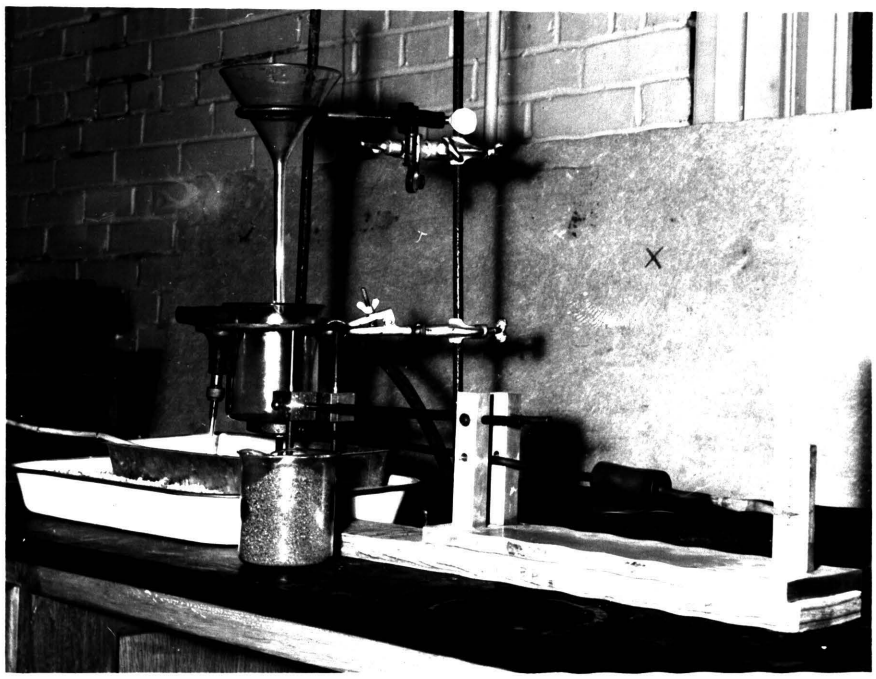

Figure 11. Apparatus for beam deflection tests.

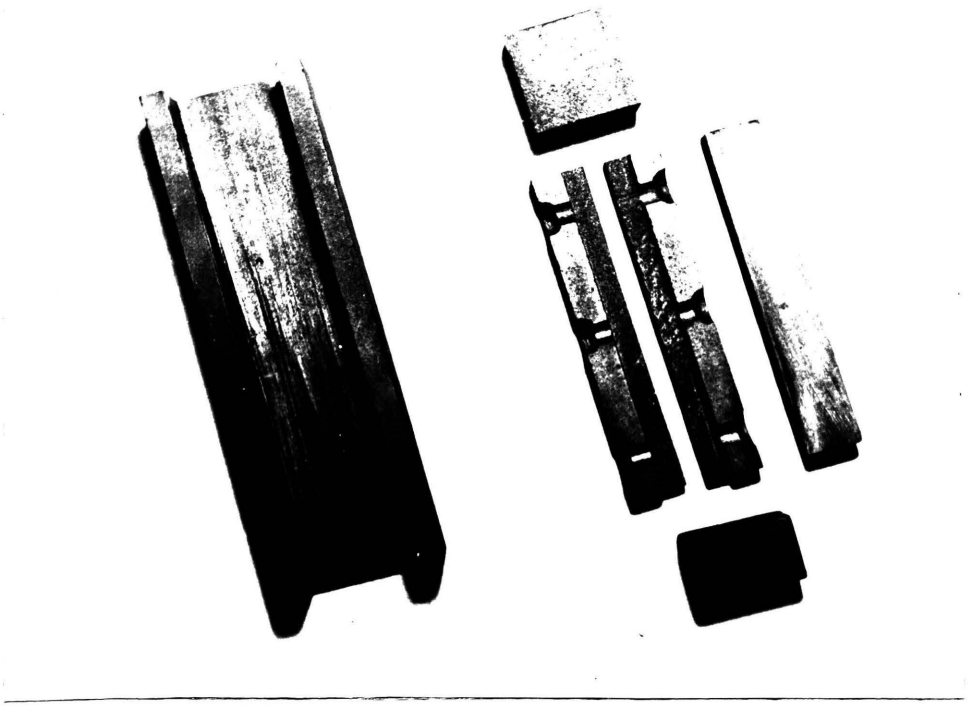

Figure 12. Graphite mold for deflection beams.

temperatures from -70° to 30°C and loaded with lead shot, which was poured through a glass funnel to maintain a definite flow rate. The load required to deflect the bar 2 mm. was then recorded. Thirty tests with three beams in each were made. The "as cast" and "as bent" beams are shown in Figures 13 and 14 respectively.

The results of the tests are tabulated in Table VII and plotted on Figure 15. Two curves were drawn; one is the average of all tests and the other is the average of the last set of ten tests which were conducted under the best loading conditions. Apparently, the recrystallization began at about -45°C and was completed at about -10°C

VI. X-RAY DIFFRACTION

The use of X-ray diffraction for the study or recrystallization is accomplished by determining the change in orientation of certain planes of the crystal lattice. This is most easily done by comparing the X-ray line intensities for those planes before, during and after recrystallization. To do this for indium, a special specimen holder was constructed for the Norelco X-ray spectrometer in the Metallurgy Department which had provision for keeping the specimen in a dry ice and acetone bath during irradiation. Figures 16 and 17 show the specimen holder and the holder mounted on the spectrometer.

The procedure for the experiment was to cold work a specimen, place it in the specimen holder at a temperature of -70°C and scan the geiger tube back and forth across the line for the plane to be studied while the temperature is allowed to rise. If the plane

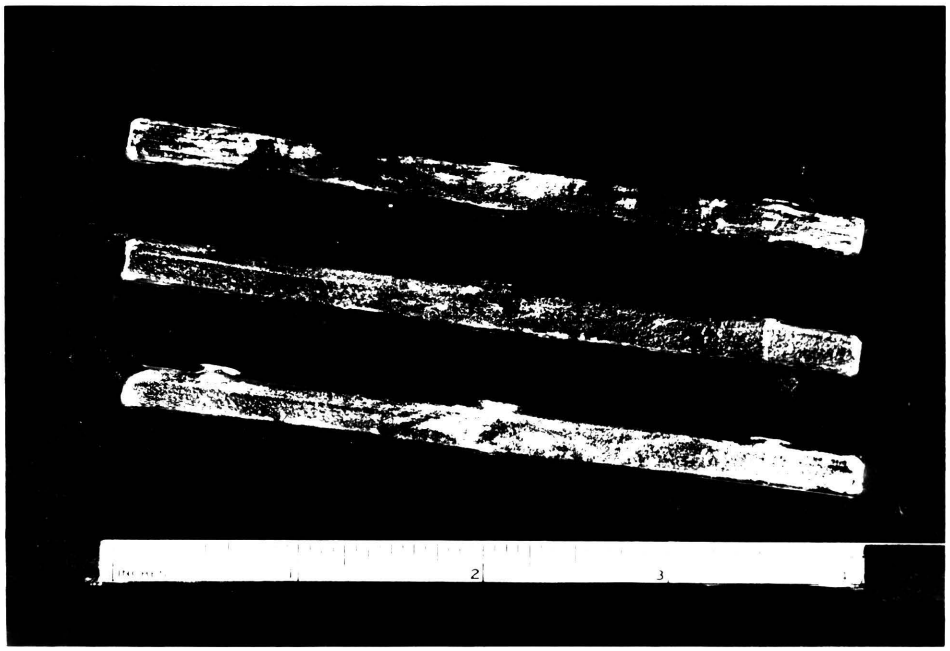

Figure 13. As cast deflection beams.

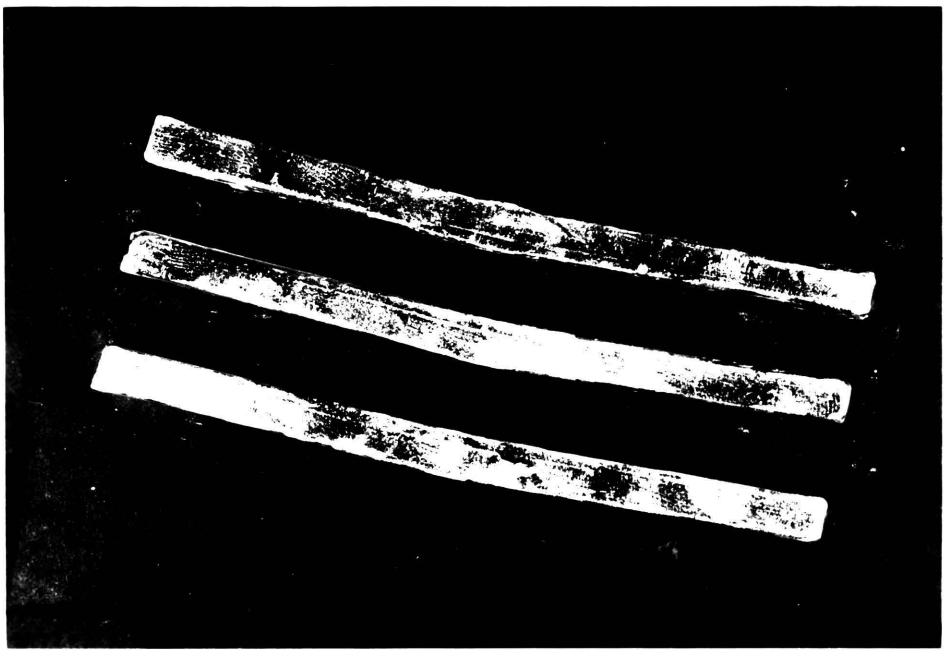

Figure 14. Bent deflection beams.

TABLE VII

LOAD TO DEFLECT BEAM 2 MM. VERSUS TEMPERATURE

Temperature in °C	Load in grams	
	Ave. of all tests.	Ave. of 10 best tests
-70	1759	1791
-60	1657	1694
-50	1690	1724
-40	1660	1541
-30	1458	1446
-20	1388	1342
-10	1213	1263
0	1177	1229
10	1191	1191
28	969	1005

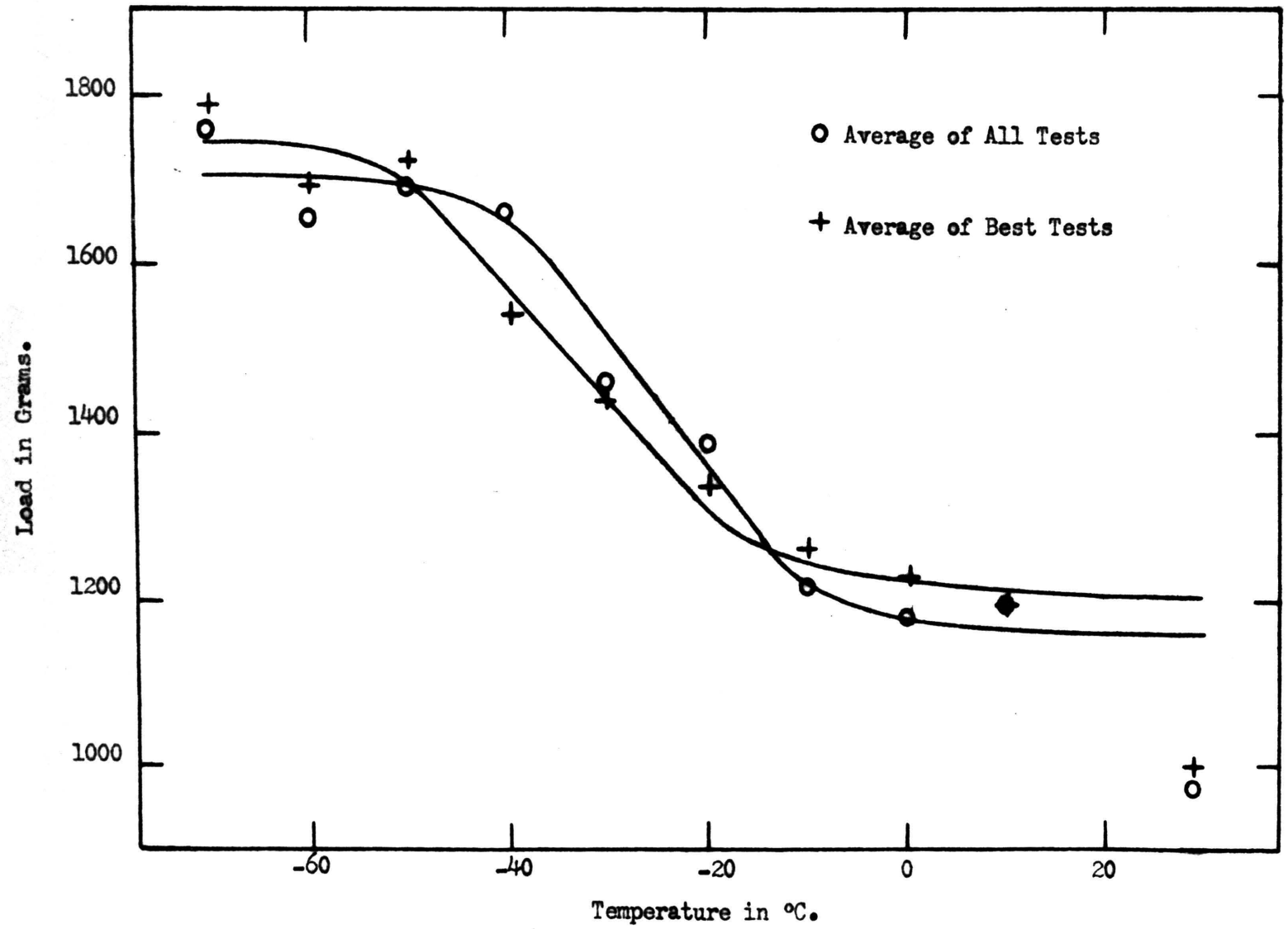

Figure 15. Effect of recrystallization on the bending strength of indium.

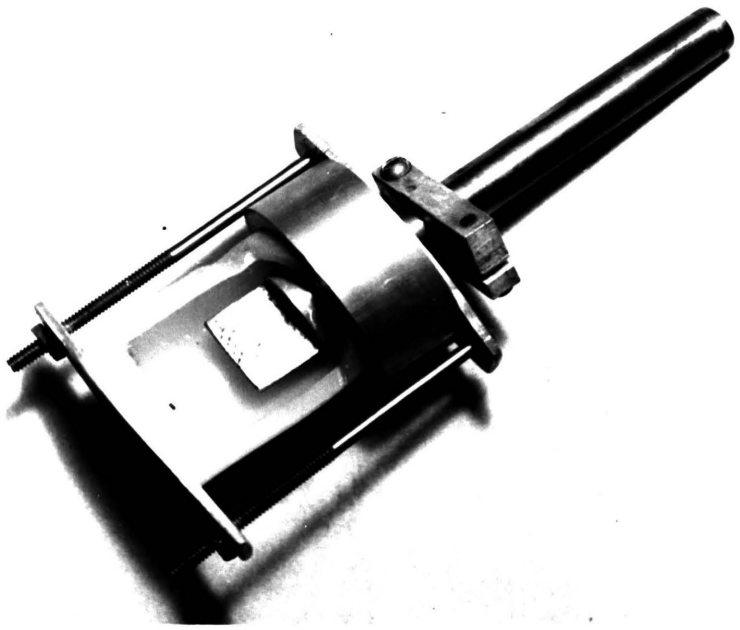

Figure 16. Special specimen holder for Norelco spectrometer.

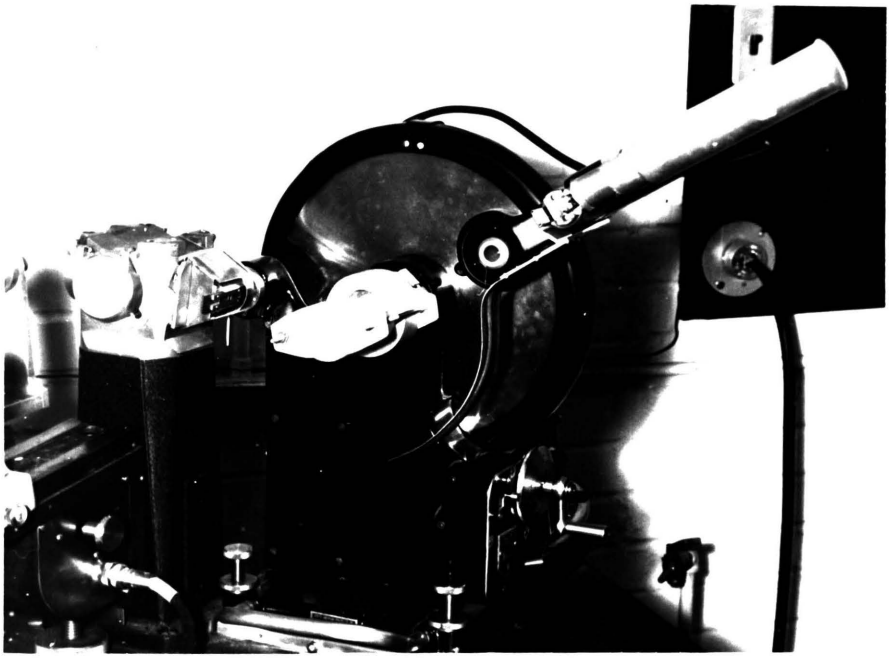

Figure 17. Specimen holder in place on spectrometer.

observed was one which showed a change in orientation, it would be evidenced by a change in the relative line intensity.

In accordance with the above procedure, a specimen of indium was rolled to an 80% reduction while trying to maintain the specimen temperature at less than -70°C. The specimen was then placed in the specimen holder with the bath at -70°C and the Geiger tube set to scan back and forth over the line for the (111) plane. The diffracting angle for the various planes were obtained from the diffraction pattern described in Chapter III. The intensities resulting, as the temperature of the bath increased, were recorded on the chart recorder accompanying the spectrometer. Figure 18 is a plot of the relative intensities of the (111) plane as the temperature increased. Because of the small size of the bath, the temperature increased very rapidly and the lower temperature part of the curve was not obtained. The curve seemed to indicate that recrystallization was completed at about -5°C.

According to the above curve, the (111) plane seemed to be suitable for further work. As a consequence it was then used in an attempt to determine the activation energy of recrystallization. The first step in the procedure was to obtain a number of curves at different temperatures within the recrystallization range of intensity versus time of annealing. In accord with this idea, a series of cold rolled specimens were annealed at -30° $\pm$ 1°C for 0, 2, 4, 8, 15, 30 and 60 minutes each. The results of this test appeared to indicate that the annealing times were not long enough at this temperature so

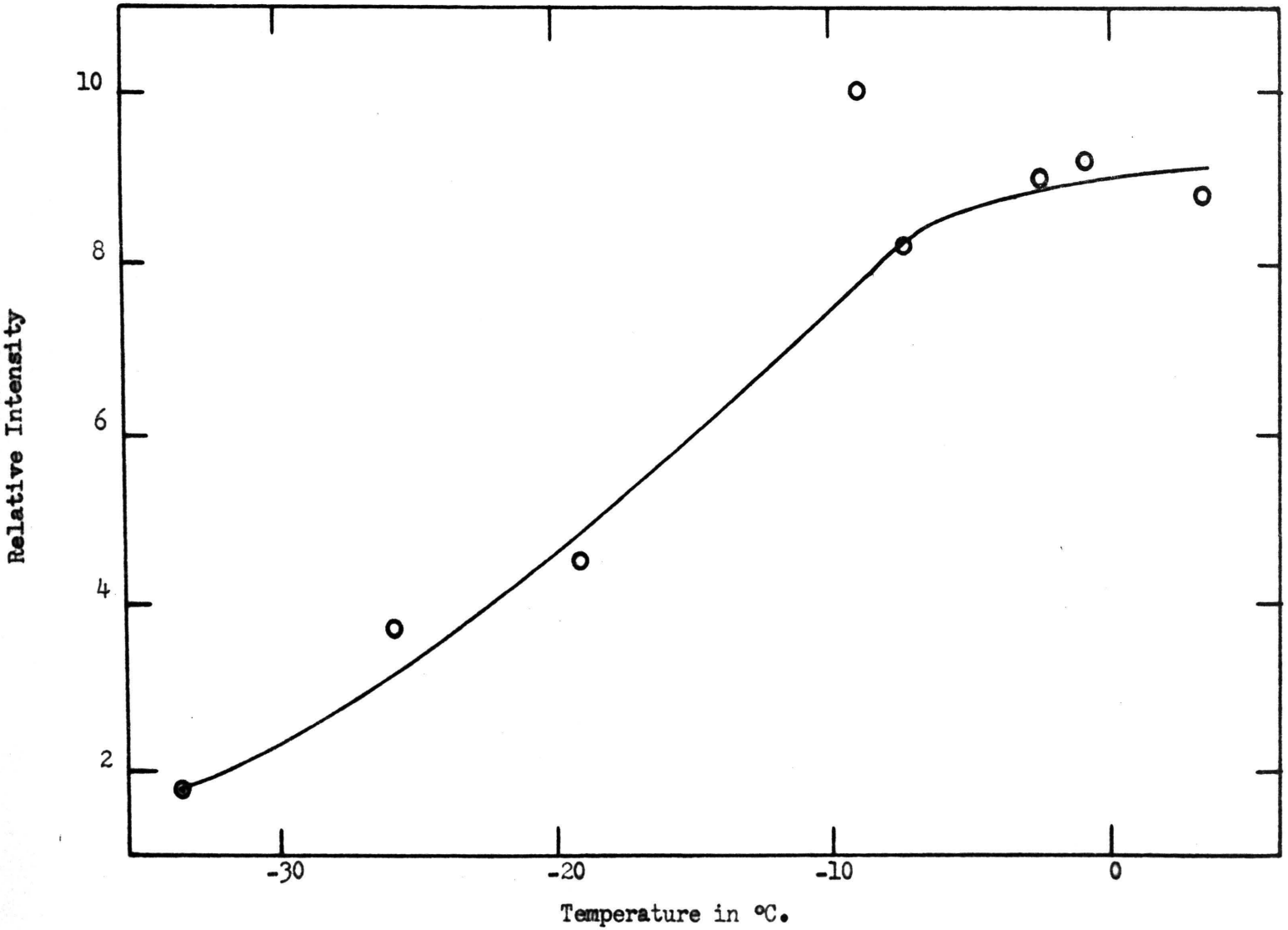

Figure 18. Effect of recrystallization on the relative intensity of the X-ray diffraction from the (111) plane.

another check was run at -20° ± 1°C with annealing times from 2 to 240 minutes. The results of this test were too erratic for the construction of a suitable curve. Checks were made on the other diffraction lines for the planes, (002), (200), (202) and (222) with equally discouraging results. As a consequence, it was decided to abandon this phase of the work. Some of the variables that were affecting the results were specimen position, level of acetone in the bath and the difficulty of maintaining temperature in such a small bath. Because of the results of the latter part of the test, the curve on Figure 18 is of dubious value. For work of this nature a low temperature fixture employing liquid nitrogen or some other liquid gas would probably work better.

VII. METALLOGRAPHY

The use of metallography to study recrystallization is one of the most powerful methods. Its application to the investigation of indium was rather difficult though because of the necessity of etching a sample at -70°C. Most etchants are very inactive at those temperatures. A number of etchants were tried, and concentrated hydrofluoric was the only one which was effective even though the 48% solution used froze at -70°C. Three samples of indium were prepared by cold rolling to an 80% reduction at -70°C and then treated as follows:

a. immersed in hydrofluoric acid at near -70°C and held there for five minutes, after which the etchant was allowed to melt and the specimen removed, washed in water and dried.

b. annealed at -30°C for 1/2 hour and etched as above at -30°.

c. annealed at room temperature for at least 1/2 hour and etched in hydrofluoric until grain boundaries were revealed.

Figures 19, 20 and 21 show the result of the experiment. The photomicrographs in Figures 19 and 20 were taken at 650X and the grain boundaries are barely discernible. Figure 20 shows a definite indication of equiaxed grains which appear to be absent in Figure 19. Figure 21 on the other hand at 100X shows all equiaxed grains. Interpretation of the Figures indicates that recrystallization has taken place at or below -30°C. The method was not decisive enough to encourage further investigation.

In conclusion we can say that regardless of the total amount of cold work, as long as there is some, recrystallization will begin below -40°C and be completed below 0°C. With severe cold work the beginning temperature is probably somewhere in the vicinity of -110°C with completion at about -70°C.

Figure 19. Indium sample, cold worked and etched in HF at -70°C, longitudinal.

Figure 20. Indium sample, cold worked at -70°C, annealed and etched at -30°C in HF, longitudinal.

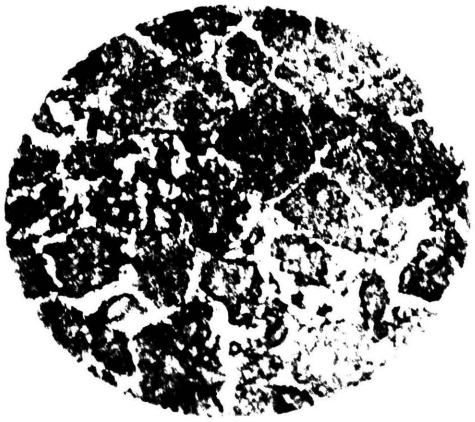

Figure 21. Indium sample, cold worked at -70°C, annealed at room temperature and etched in HF, longitudinal.

CHAPTER VI

HARDNESS OF INDIUM

The hardness of indium is rather difficult to measure accurately because of the tendency for the metal to creep under load. C. Rubenstein studied the effect of creep on hardness measurements and concluded that the Meyer hardness interpretation was not applicable to indium for this reason.[71],[72] Accordingly, all the tests in this study were made at very low loads.

A Brinell test was made first. Three samples of indium, 1/2" x 5/8" x 1 1/4", were cast in graphite. They were indented by use of a chemical balance which held the sample against a 10 mm. ball with a load of 5 kg. for 30 seconds. The diameters of the impressions, as measured by a Brinell microscope, were 2.80, 3.05 and 3.00 mm. which computed to an average Brinell hardness of 0.72 by the formula:

$$B.h.n. = \frac{P}{\frac{\pi D}{2}\left(D - \sqrt{D^2 - D_1^2}\right)}$$

where P is the load in kg., D is the diameter of the ball in mm. and D_1 is the diameter of the impression in mm.[73]

The next tests were made on a Tukon Micro-Hardness Tester. The specimen was a polished sample of indium mounted in bakelite. All tests were made within grains and not across grain boundaries. First

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[71]Rubenstein, loc. cit.

[72]Meyer, loc. cit.

[73]George L. Kehl, Metallographic Laboratory Practice (third edition; New York: McGraw-Hill Book Company, 1949), p. 220.

three tests were made with a Knoop indenter under a 25 gm. load. The average of the three tests was 1.197 as computed by the following formula:

$$KHN = \frac{P}{C_p l^2}$$

where KHN is the Knoop hardness number, P is the load in kg., C_p is the Knoop indenter constant, 0.07028, and l is the length in mm.[74]

Next three tests were run with a diamond pyramid hardness indenter under a 100 gm. load. The average of these three tests was 1.266 as calculated by the formula:

$$DPH = 1.854 \frac{P}{D^2}$$

where DPH is the diamond pyramid hardness number, P is the load in kg. and D is the average length of the two diagonals in mm.[75]

And finally a series of tests were made employing a Bergsman Micro-Hardness Tester. The same polished and mounted indium sample was used. A DPH indenter was loaded with loads of 5, 10 and 25 gm. for 15 seconds each, three tests at each load. The average results for each of the three loads were 1.389, 1.402 and 1.240 respectively as computed by the DPH formula. The 25 gm. load in these tests was too heavy as the specimen could be seen to creep away from the penetrator before the tests were completed.

The complete data for these tests is given in Table VIII. Summarizing, the hardness of indium is 0.72, Brinell, 1.197, Knoop, and

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[74] Ibid., p. 248.

[75] Ibid., p. 228.

TABLE VIII

DATA FOR HARDNESS TESTS

Brinell Test, 10 mm. ball, 5 kg. load

Sample No.	Diam. of Impression in mm.		Bhn.
1	2.80		0.80
2	3.05		0.66
3	3.00		0.69
		Ave.	0.72

Tukon Micro-Hardness Test
Knoop indenter, 25 gm. load

Test No.	Length of Diagonal in mm.		KHN
1	0.507		1.383
2	0.556		1.152
3	0.581		1.057
		Ave.	1.197

DPH indenter, 100 gm. load

Test No.	Ave. of 2 Diagonals in mm.		DPH
1	0.403		1.142
2	0.366		1.384
3	0.382		1.271
		Ave.	1.266

Bergsman Micro-Hardness Test
DPH indenter, 5 gm. load

Test No.	Ave. of 2 diagonals in mm.		DPH
1	0.0782		1.514
2	0.0918		1.100
3	0.0773		1.552
		Ave.	1.389

TABLE VIII (continued)

DPH indenter, 10 gm. load

Test No.	Ave. of 2 Diagonals in mm.	DPH
1	.1132	1.449
2	.1161	1.377
3	.1160	1.379
		Ave. 1.402

DPH indenter, 25 gm. load

Test No.	Ave. of 2 Diagonals in mm.	DPH
1	0.1936	1.237
2	0.1897	1.288
3	0.1970	1.196
		Ave. 1.240

1.266 to 1.402 DPH. The Brinell values are definitely lower than those of other workers, 1.19 by Kurnakow and Zunczuzny and 0.9 by Jaffee and Weiss.[76,77] The reason for this is probably the higher purity indium used in this investigation. The DPH values on the other hand are higher than that of the National Bureau of Standards, 1.0.[78] Their indium was of 99.9% purity, but was tested under a 200 gm. load which probably resulted in some creep and a correspondingly low value.

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[76]Kurnakow and Zunczuzny, loc. cit.

[77]Jaffee and Weiss, loc. cit.

[78]National Bureau of Standards, loc. cit.

CHAPTER VII

TENSILE STRENGTH OF INDIUM

The tensile strength of indium was determined as part of this investigation because of the misinterpreted value reported by Ludwick and Mellor.[79,80] Later investigators gave apparently correct values but gave no details as to the testing conditions.[81,82]

The small amount of indium on hand and the low loads to be used made the use of standard testing machines rather impractical. Consequently, a method was devised using a bucket loaded with lead shot as shown in Figure 22. The lead shot was fed into the bucket by the use of two glass funnels. The lower and smaller funnel was used to obtain a definite flow rate and the upper and larger funnel as a reservoir for the shot. This feeding arrangement, which is not shown in Figure 22 had a flow rate of 8.6 pounds per minute.

Three bars of 3/8 inch diameter were cast in preheated graphite molds. The type of mold used is shown in Figure 23. The bars were then pulled using the loading rate as given above, and the tensile strength, elongation and approximate reduction in area calculated.

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[79]Ludwick, op. cit., p. 14.

[80]Mellor, loc. cit.

[81]National Bureau of Standards, loc. cit.

[82]Jaffee and Weiss, loc. cit.

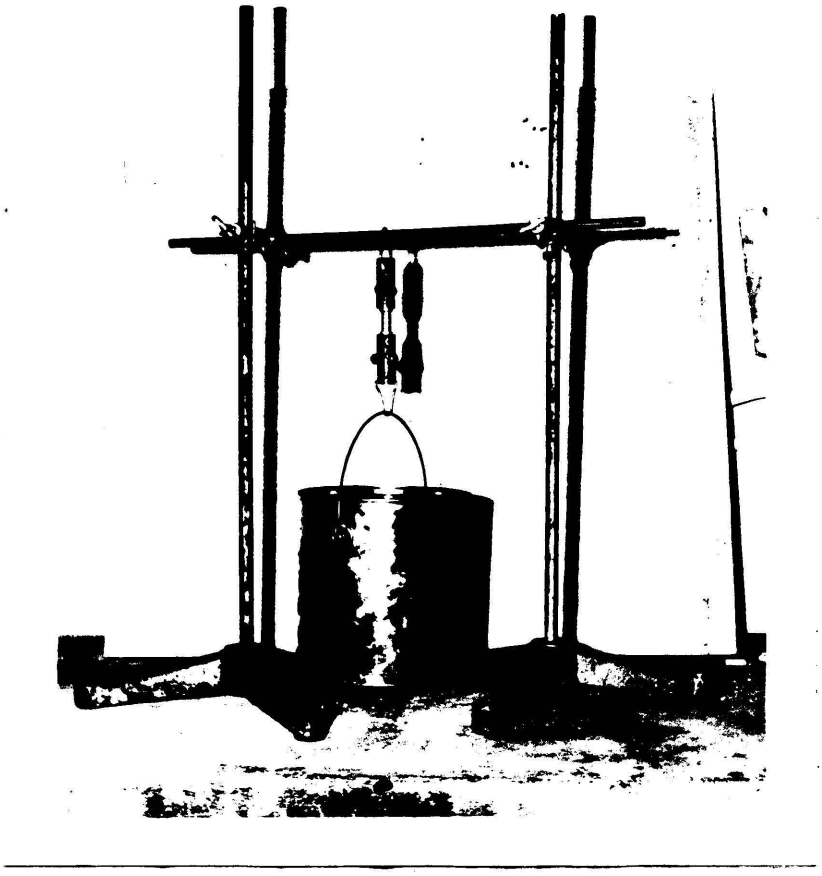

Figure 22. Loading device for tensile tests.

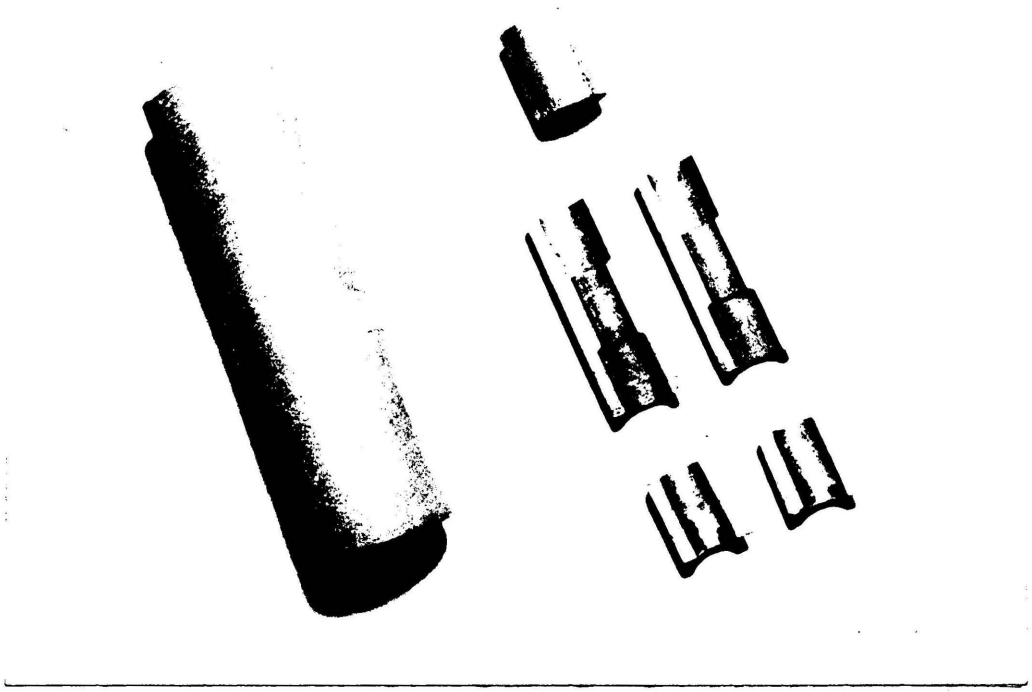

Figure 23. Graphite molds for tensile bars.

A definite loading rate was necessary because of the appreciable creep of the indium during the tests. The results of the stress rupture tests in Chapter VIII bear out this phenomena conclusively.

The conditions and results of the tests are tabulated in Table IX, and the appearance of the bars before and after testing is shown in Figures 24, 25 and 26. Figure 24 is the as cast bars, Figure 25 is the as pulled bars, and Figure 26 is the appearance of the fractures of the bars. The average results are a tensile strength of 388 psi., an elongation of 70% and an approximate reduction in area of 95%. From the appearance of the fractures and the fact that the higher values of cast bars are probably more representative of the true material, the values for bar no. 3 of 410 psi tensile strength, 72% elongation and 100% reduction in area are probably the best values.

For a comparison of these results with other recent data, see Table X. The National Bureau of Standards values are in fair agreement with this work and seem to be reasonable.[83] The low elongation and reduction in area, 22% and 87% respectively of Jaffee and Weiss are definitely out of order, and it is difficult to justify the differences without knowing more about their testing procedure and the purity of their indium.

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[83] National Bureau of Standards, loc. cit.

[84] Jaffee and Weiss, loc. cit.

TABLE IX

Bar No.	Diam. in in.	Gauge length in in.	Area in sq. in.	Load in pounds	Elong. in in.	T.S. psi.	% Elong. in 8	% R. in A. (estimated)
1	0.369	0.78	0.1070	42.25	1.32	395	69	95
2	0.371	0.78	0.1080	38.75	1.32	359	69	90
3	0.370	0.78	0.1075	44.13	1.34	410	72	100
Averages						388	70	95

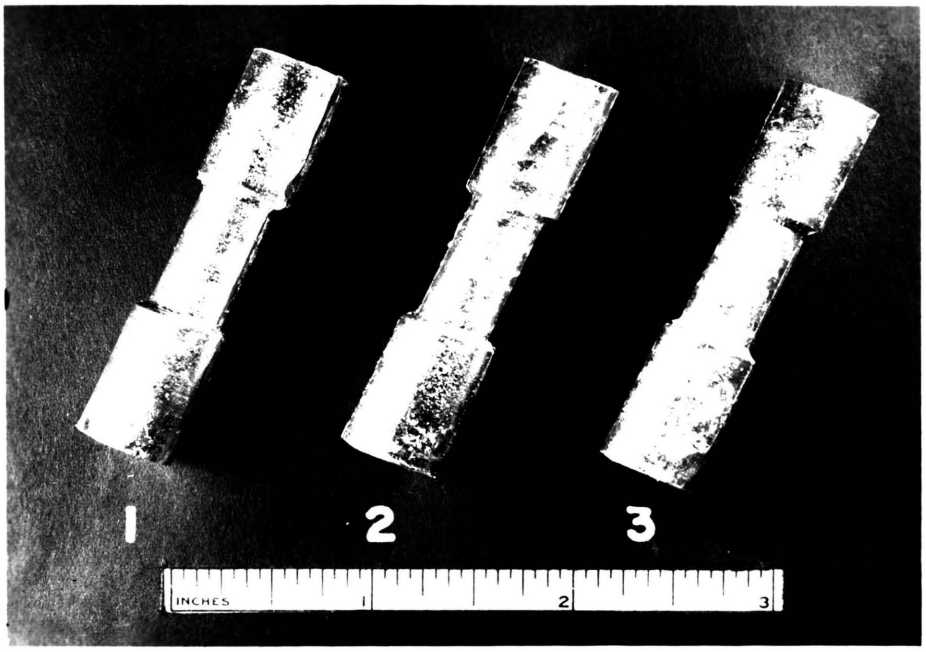

Figure 24. As cast tensile bars.

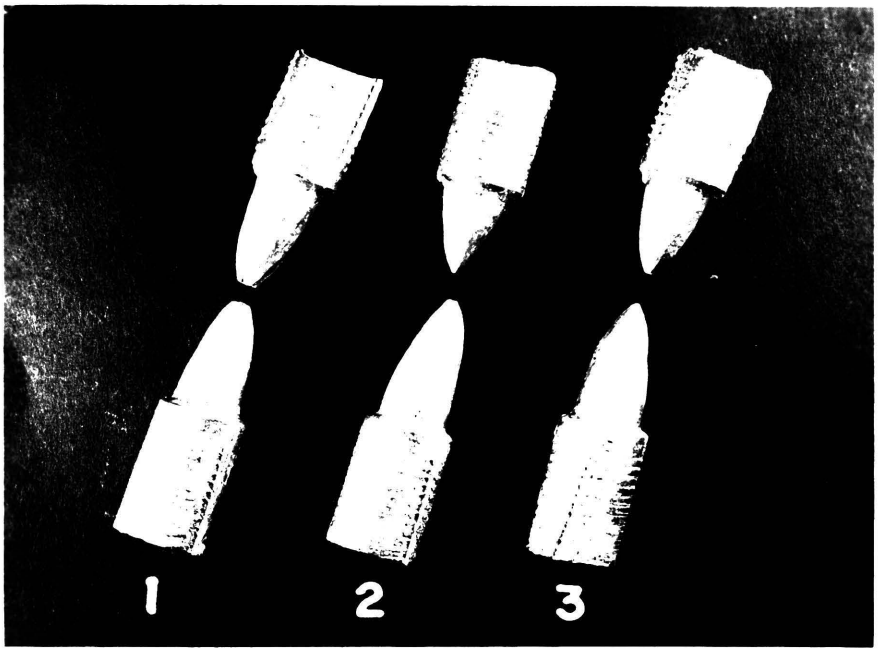

Figure 25. As pulled tensile bars.

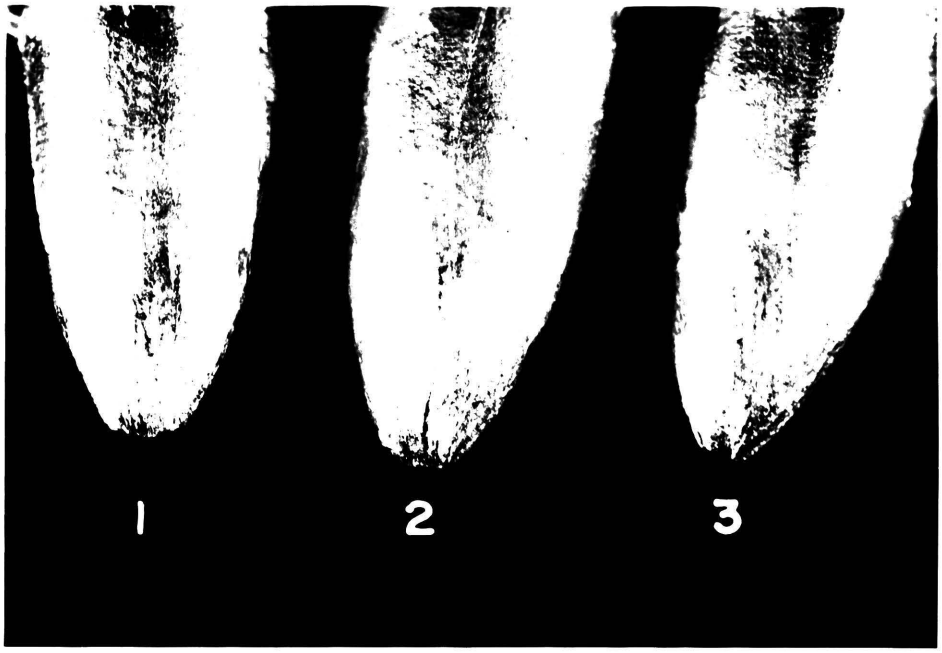

Figure 26. Appearance of the fractures of the pulled tensile bars.

TABLE X

Property	This Study	N.B.S.	Jaffee & Weiss
Tensile Strength in psi:	388	430	380
% Elongation	70	---	22
% Reduction in Area	95	99	87

N.B.S. - 99.9% indium, 3/8 " diam. cast rod.

CHAPTER VIII

Stress-Rupture Properties of Indium

Stress-rupture tests are usually run on superalloys at elevated temperatures to evaluate them for high temperature application. Tests of this nature can be run on indium at room temperature since it creeps much the same way at room temperature as the superalloys do at high temperature. The information from such tests on indium of course is purely academic and of very little practical use.

White, Clark and Wilson developed the procedure for these tests.[85] It consists of pulling specimens in tension under a constant load until they creep to fracture. The tests are usually run at elevated temperature and yield values of time for rupture as a function of varying stress. Then the stress is plotted against the time as a semi-log and log-log plot which usually give straight lines.

Thirty-eight bars of indium, cast the same as for the tensile tests, were broken under constant loads at stresses varying from 423 to 188 psi. and the times for rupture recorded. The data are tabulated in Table XI. Figures 27, 28 and 29 are plots of stress versus time, stress versus log time and log stress versus log time respectively. All plots show two curves, one for the average times to rupture and the other for the high times. The high rupture times are probably representative of the most perfect cast tensile bars tested in the best manner and are consequently a better indication of the true strength of the material.

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[85] A. E. White, C. L. Clark and R. L. Wilson, loc. cit.

TABLE XI

STRESS-RUPTURE DATA

Diam. of bar 0.369 in.
Gauge length 0.88 in.
Area of cross section 0.107 sq. in.

Load in lbs.	No. of Tests	Stress in psi.	Time in hours		Elongation in % (Ave.)
			Average	High	
45.25	6	423	0.0115	0.0162	65.5
40.25	8	376	0.0362	0.0712	62.1
35.00	6	327	0.0977	0.1842	62.7
30.19	6	282	0.261	0.557	65.2
25.25	6	236	0.930	1.662	66.3
20.125	6	188	6.99	11.37	71.6

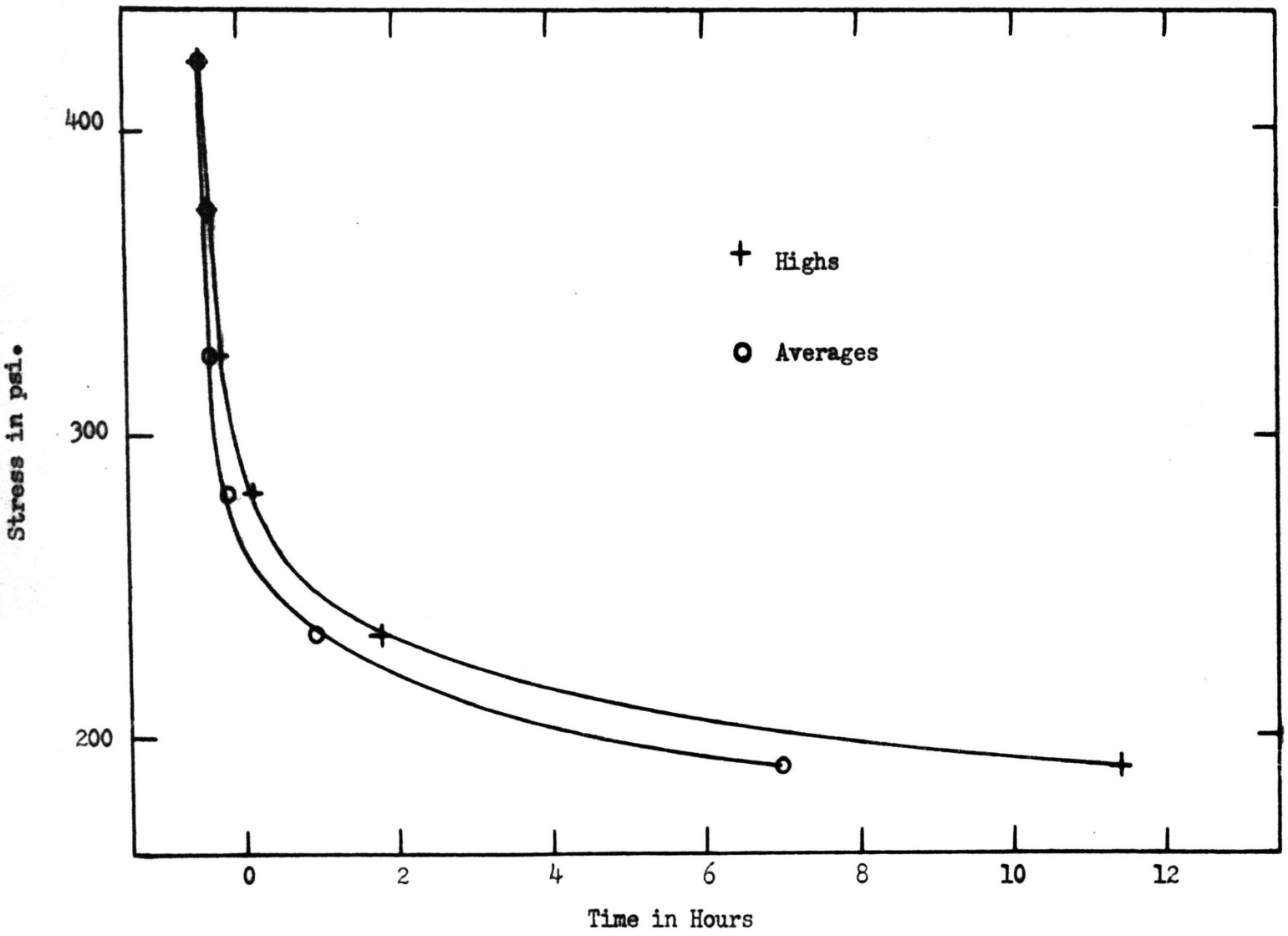

Figure 27. Rupture stress versus time to rupture

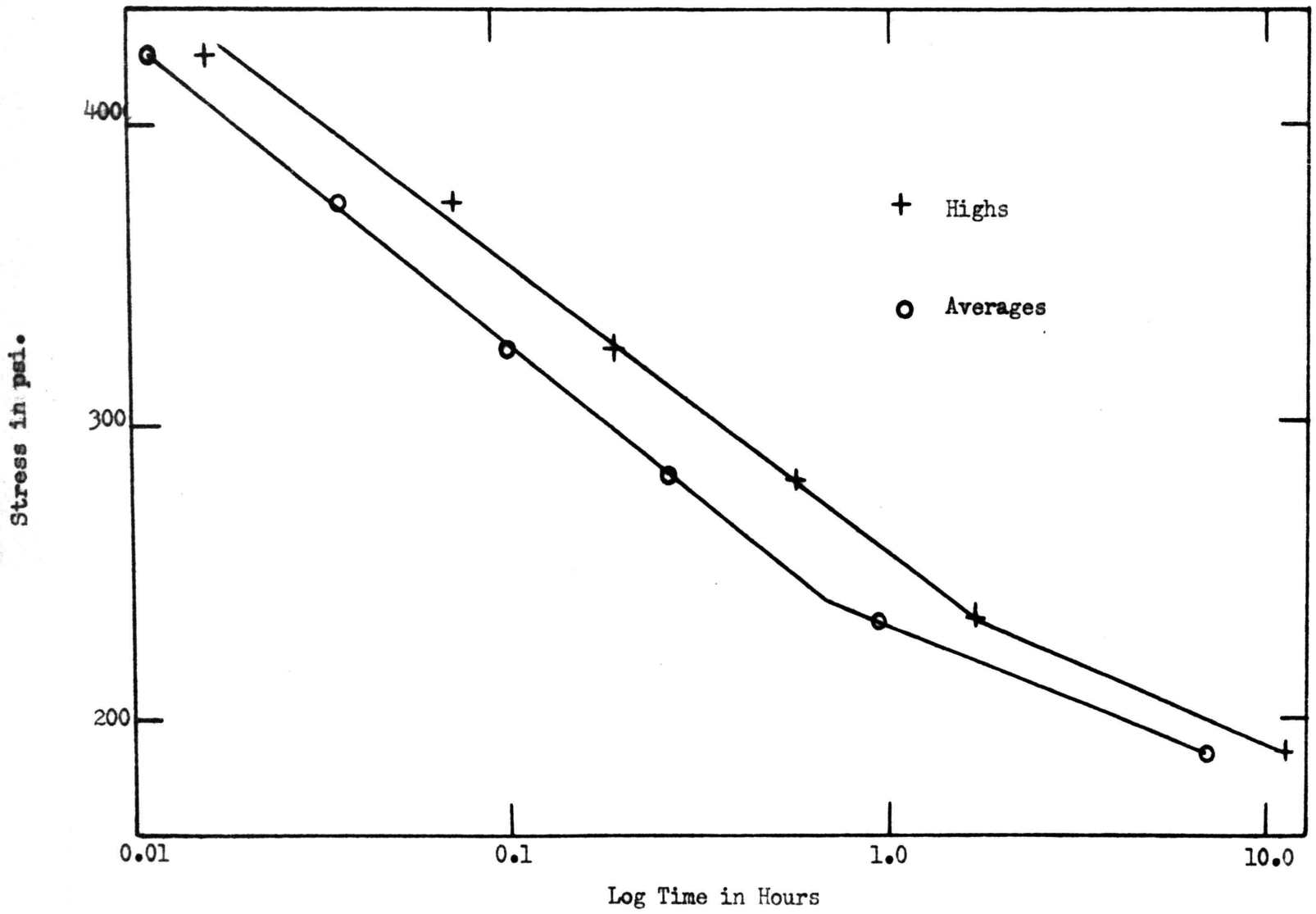

Figure 28. Rupture stress versus log time to rupture.

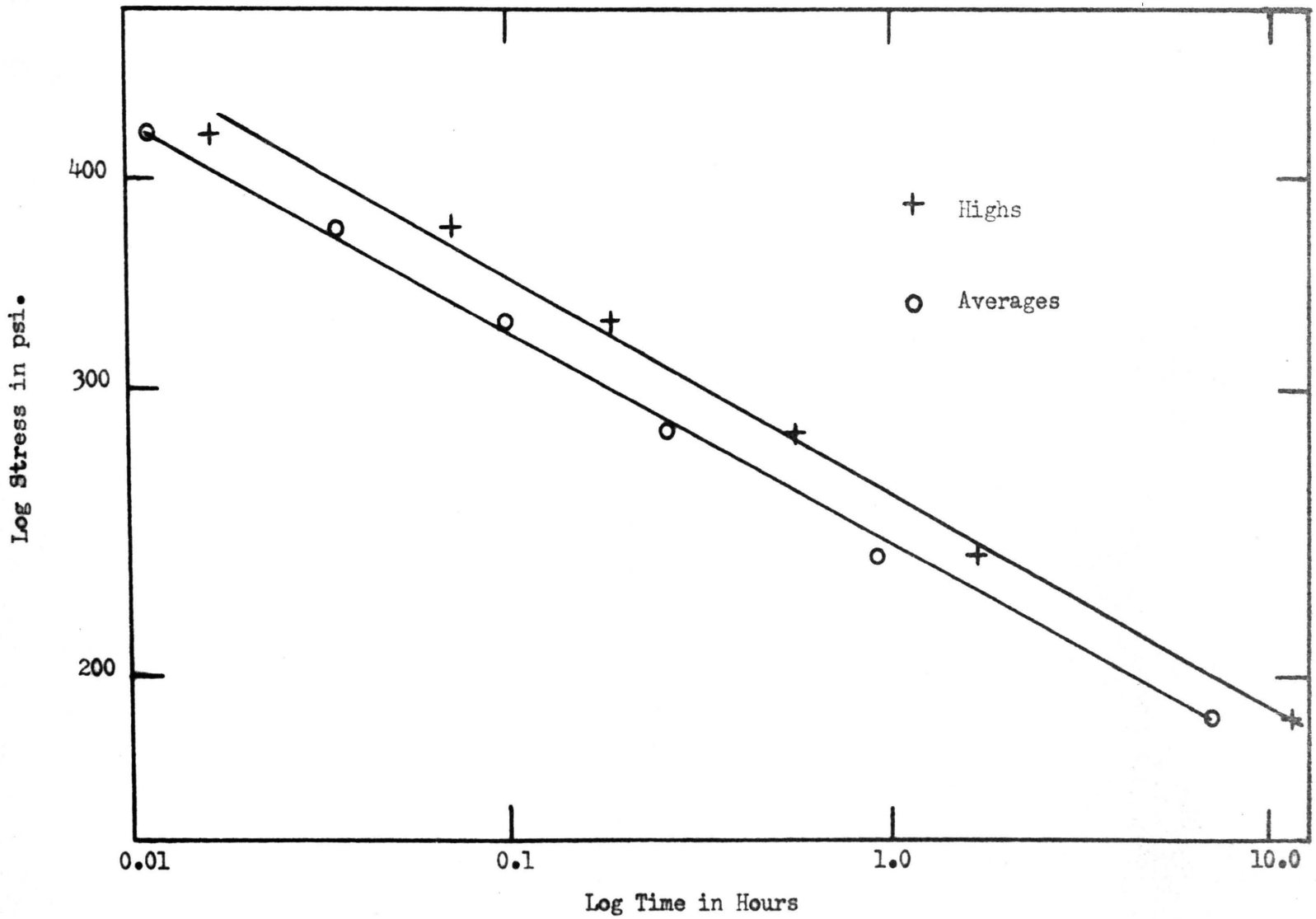

Figure 29. Log rupture stress versus log time to rupture.

The elongations were not plotted, since they followed no definite trend.

Larson and Miller suggested the use of the parameter, T(C+log t), where T is the absolute temperature of testing, t is the time to rupture and C is a constant.[86] The parameter was first used by Holloman and Jaffee in their studies on tempering steel, and is derived from the rate equation:

$$r = Ae^{-Q/RT}$$

where r = the rate, A = a constant, Q = the activation energy, R = the gas constant and T = the absolute temperature.[87] At constant stress, however, r = 1/t, where t is the time to rupture and the equation becomes:

$$1/t = Ae^{-Q/RT} \text{ (for constant stress)}$$

which can be reduced to:

$$T(C + \log t) = A/2.3R = \text{const. (for constant stress)}$$

where C = log A. Therefore if t is known at two different temperatures for a particular stress, C can be calculated. According to Larson and Miller, C equals approximately 20 for the most materials.[88] After C is evaluated, the log stress can be plotted against this parameter to

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[86]Larson and Miller, loc. cit.

[87]John H. Holloman and Leonard D. Jaffee, "Time-Temperature Relations in Tempering Steel," Transactions of the A.I.M.M.E., Iron and Steel Division, 162:227, 1945.

[88]Larson and Miller, op. cit., p. 771

produce a master rupture curve and the parameter can also be used to find different combinations of t and T which give the same stress.

To apply this parameter to indium, more data were needed at some particular stress and at a different temperature. Since the 282 psi. stress was near the median stress employed and was low enough to yield reasonable results at the higher temperature, it was chosen as the particular stress and seven bars were ruptured at 120°F. The temperature was attained by placing the entire testing mechanism in a drying oven and was maintained at 120° ± 5°F. The average and high time to rupture in hours was 0.0636 and 0.1495 respectively. These values were then used with the values obtained before at 65°F at the same stress to calculate C. C was computed to be 8.04 and 7.27 respectively for the average and high times which do not agree with the value of 20 proposed by Larson and Miller.[89] This is not too surprising though when the other properties of indium are compared to those of the superalloys for which stress-rupture data is usually calculated. Using these values of C, a master rupture curve was plotted for indium on Figure 30.

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[89] Ibid.

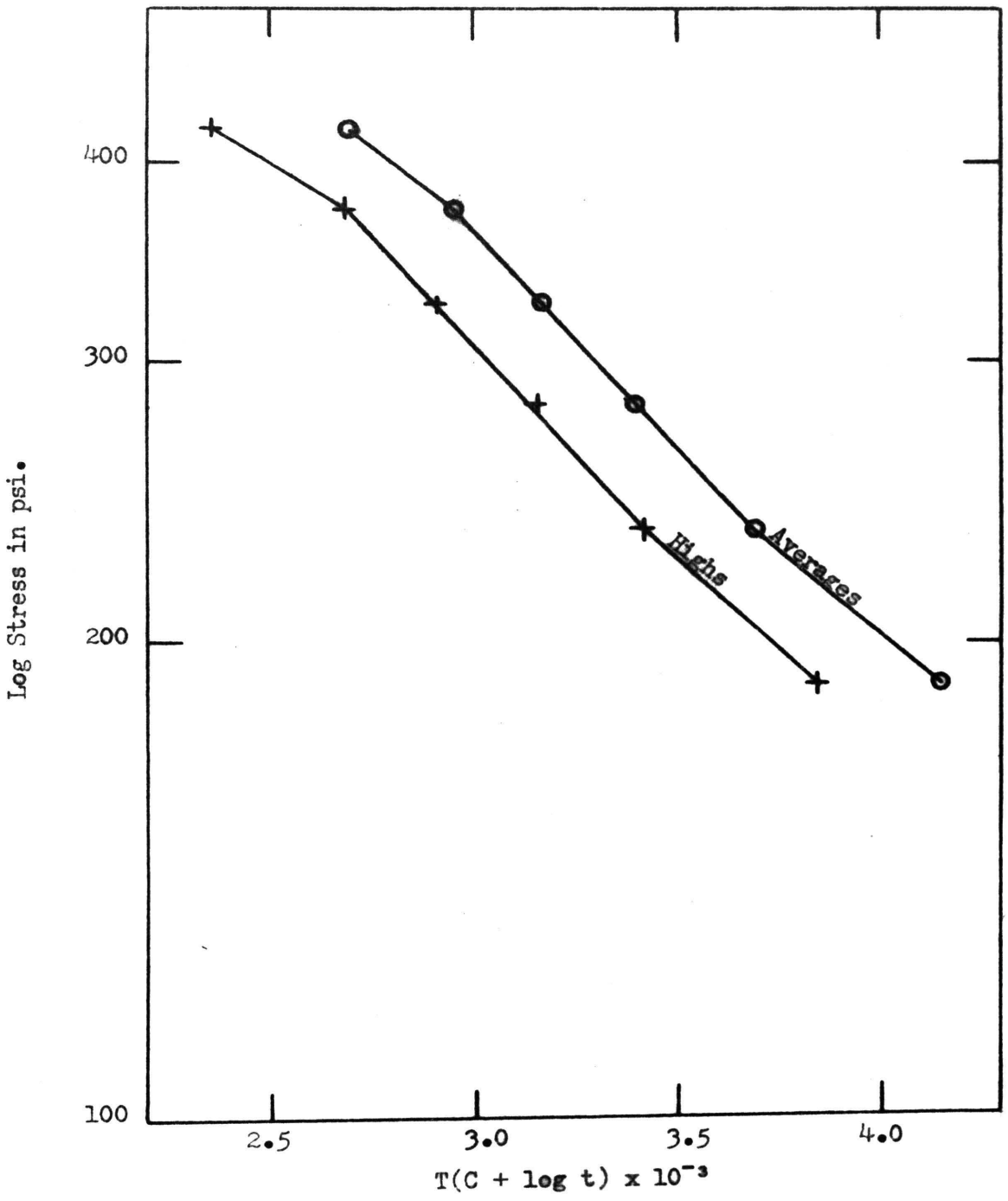

Figure 30. Master rupture curve for indium.

CHAPTER IX

SUMMARY AND CONCLUSIONS

Three major items resulted from this investigation of indium. They were the development of new metallographic techniques, the determination of the recrystallization temperature and the re-examination of some of the mechanical properties.

Aqua regia as an etchant for indium was employed both to remove the disturbed metal surface from the polishing and grinding and to reveal twinning and differences of crystal orientation. The microstructures obtained with this etchant were superior to those obtained with the 50% nitric acid and water, the Vielle's reagent, the hydrochloric acid and potassium chlorate, and electrolytic etch used in previous investigations.

The use of an etch-cutter to prepare strain-free surfaces for micro-examination was also an improvement. Other methods involved mechanical working of the surface and consequently resulted in a recrystallized microstructure. With the etch-cutter followed by careful final polishing, true microstructures could be prepared.

The effect of recrystallization on electrical resistance, thermoelectric force, hardness, resistance to bending deflection, crystal orientation and microstructure were studied with varying degrees of success. The results were a range for recrystallization over about 40°C., beginning at about -110°C. for severe cold work and at about -40°C. for slight cold work.

The hardness of indium was checked by Brinell and two different micro-hardness methods, Tukon and Bergsman. The Brinell hardness was 0.72; the Knoop hardness, 1.197; and the Diamond Pyramid Hardness, 1.266 to 1.402.

The tensile strength, elongation and reduction in area was determined for a 3/8 inch diameter cast indium bar at a loading rate of 8.6 pounds per minute. They were 388 psi., 70% and 95% respectively. An extension of the tensile tests to obtain stress-rupture data resulted in the plotting of a master rupture curve for indium.

Other less important results of the investigation were the development of techniques for the growing of indium single crystals and the strain-free cutting of these crystals. A horizontal, moving-gradient tube furnace was employed to grow the crystals and an etch-cutter was used for the cutting.

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APPENDIX A

APPENDIX A

CONSTRUCTION OF THE CRYSTAL FURNACE

To grow single crystals of indium, a special furnace had to be constructed. The unusual characteristics needed to grow crystals necessitated it.

I. GENERAL REQUIREMENTS

A furnace was required which would provide a heating zone that could be moved along a tube, at varying rates of travel. Construction of a furnace of this type had been started by James L. Hickernell, an undergraduate student in the Metallurgy Department. The author merely finished his work. First a wooden frame was built to hold the various components. Figures 31 and 32 show the general arrangement of the equipment. The construction of the heating unit, drive mechanism, controls, furnace tube suspension and the operating characteristics will be discussed in that order.

II. HEATING UNIT

The heating unit was a wire wound electrical resistance type, wound on an alundum core 3 1/2 inches in diameter and 12 inches long. The wire used was Kanthal A, 16 gauge, with a surface rating of 6 watts per sq. in. at 1300°C. A 2000 watt load was estimated to be necessary, which required 174 ft. of this wire. The core only had a capacity of 32 ft. in turns of wire so the wire was coiled in 1/4 inch coils so that the full 174 feet could be compressed into this length. The

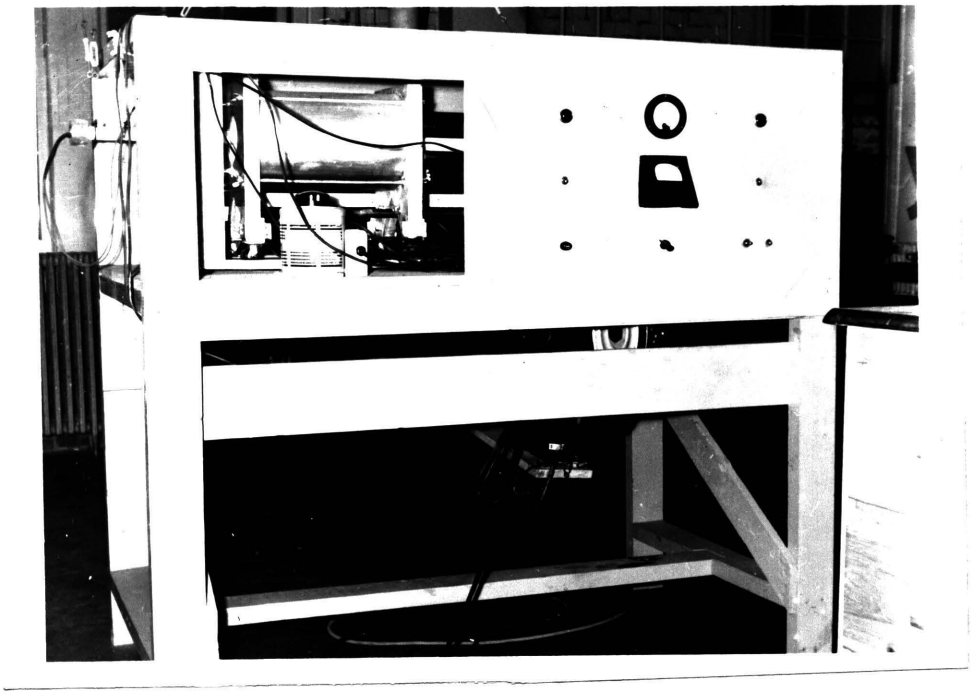

Figure 31. Front view of crystal furnace assembly.

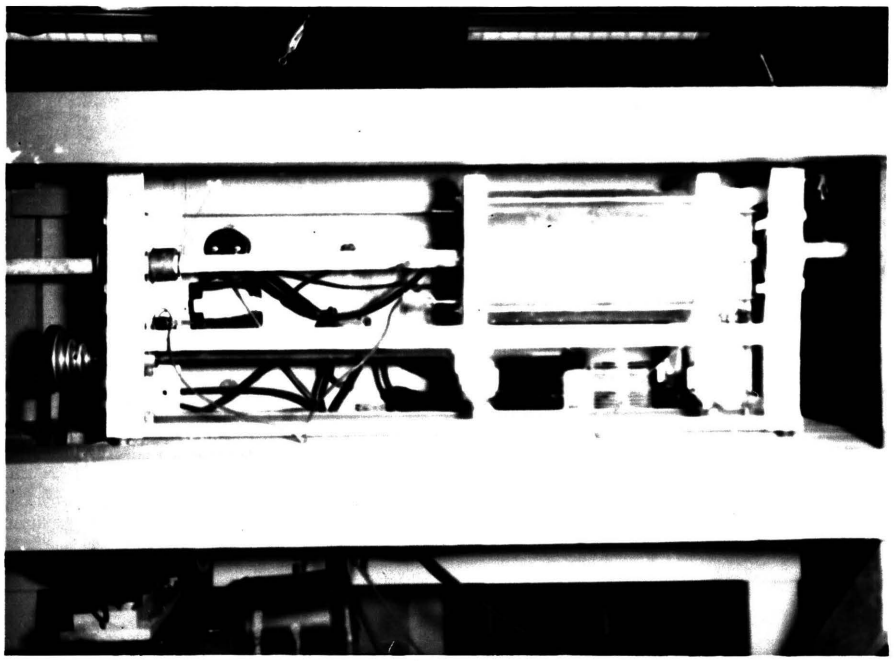

Figure 32. Back view of crystal furnace assembly.

coiled wire was then wrapped around the core, clamped, and cemented in place with alundum cement. Next the entire assembly was placed in the furnace shell which is shown in Figure 33 and the space around the core was filled in with pieces of broken insulating brick.

III. THE DRIVE MECHANISM

To move the heating unit a mechanism was needed which provided a number of constant speeds of travel. One was devised using an electric motor, two gear reducers, a screw, four V-belt pulleys and two V-belts. The starting point in the drive train was a 1/8 H.P., 1725 R.P.M. electric motor, which through a belt drive, drove a 48:1 gear reducer. This reducer in turn drove, by direct coupling, a 28:1 gear reducer. The second reducer drove a 10 thread per inch screw through a belt drive employing two 4-step pulleys. The screw in turn drove a nut which was welded to the carriage on which the furnace shell road. The carriage, constructed by welding four casters to the end frames of the furnace shell, ran on a track along the length of the furnace tube. By changing the pulleys and belts in this drive train, eight different furnace travels between 0.9 and 16 inches per hour were possible. Figure 34 shows some of the features of this drive.

IV. THE CONTROLS

Provision had to be made to control the drive mechanism and record and control the furnace temperature. This was done by the wiring

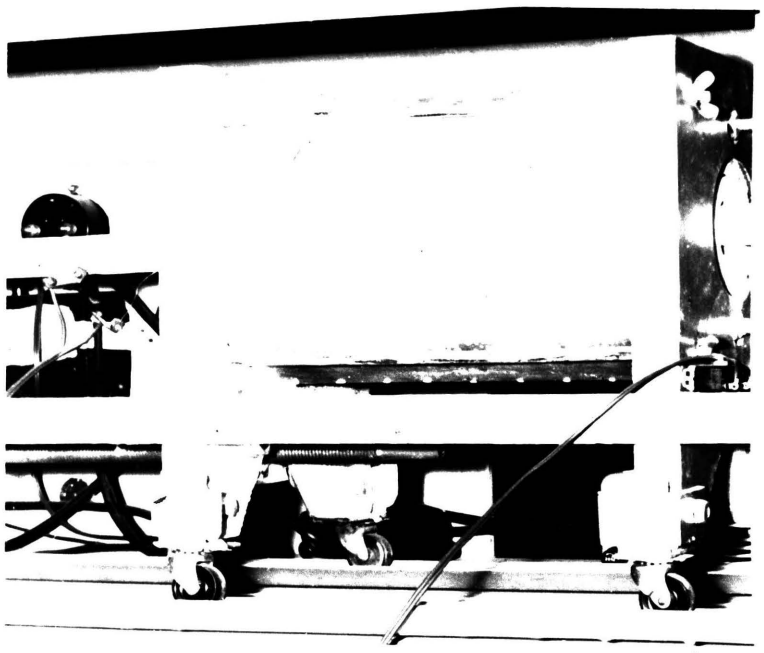

Figure 33. Furnace Shell.

Figure 34. End view showing drive mechanism.

circuit shown in Figure 35. 110 volts A. C. was supplied through main power switch, S_1, to the drive motor, the furnace auto-transformer and the temperature controller. The main features of the drive motor circuit were two microswitches, M.S. 1 and M.S. 2, which were situated at each end of the track to stop the motor at the end of the furnace travel and a reversing switch, S_4, which changed the direction of travel of the furnace by changing the current flow in the starting winding of the drive motor. Switch, S_2, supplied power to this circuit, and S_3 was used to short out the microswitches after the motor had been reversed in order to drive the furnace away from the stop at the end of the track.

The power to the furnace winding was supplied through the auto-transformer and switch, S_5, and controlled by a Brown Potentiometer type recorder-controller. An ammeter in the circuit measured the current in the secondary circuit. The controller was actuated by e.m.f. from a chromel-alumel thermocouple placed near the furnace winding and operated microswitch, M.S. 3, which provides on-off control of the furnace power. A separate thermocouple pyrometer was used to measure the temperatures of the boat in which the crystals were grown.

V. Furnace Tube Suspension

Two different size tubes were employed in the furnace. First a three inch diameter porcelain tube was used, the ends being supported by foam rubber. This tube was too large and the suspension was not free of vibration. To overcome these difficulties, a one inch diameter

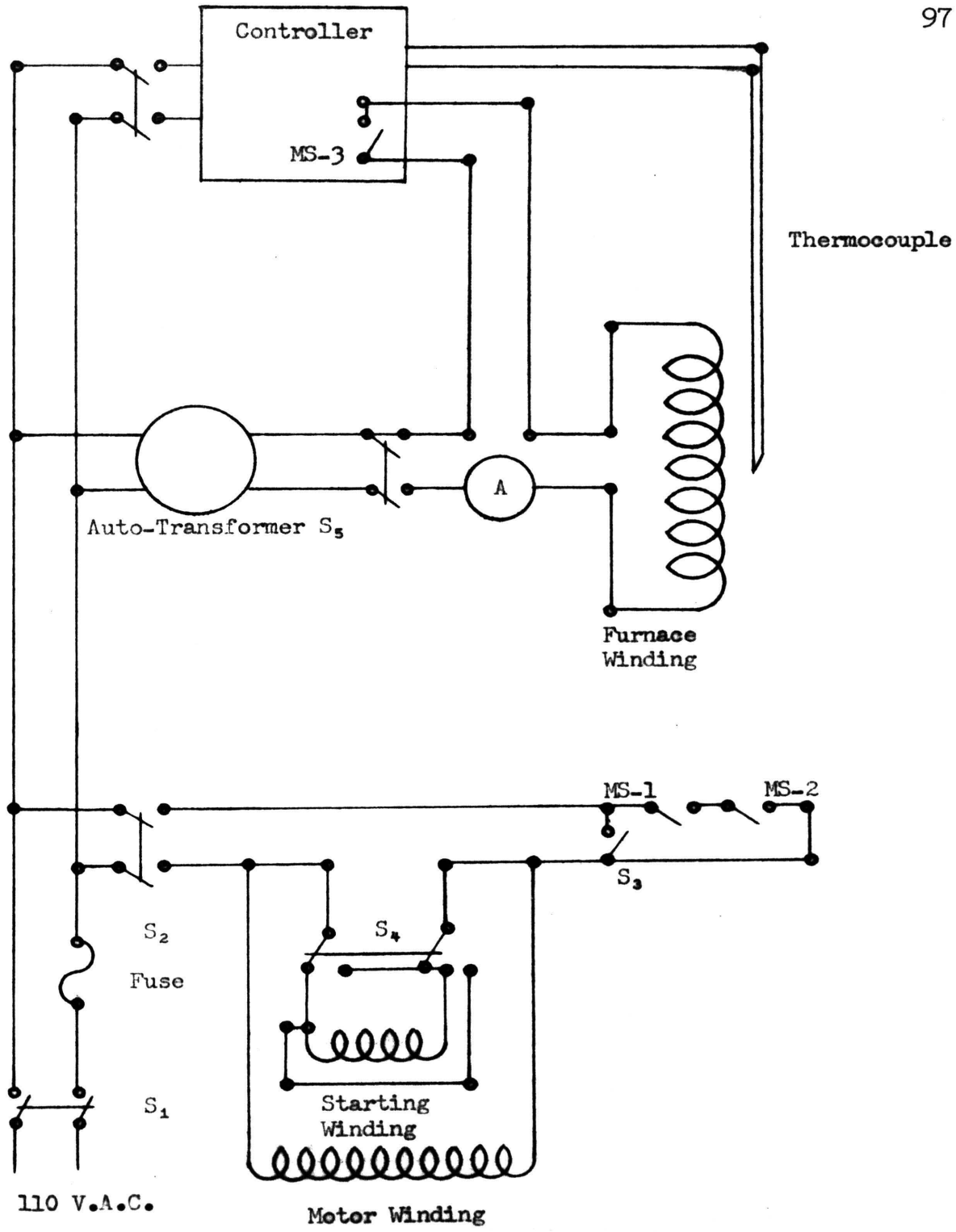

Figure 35. Wiring diagram for the crystal furnace.

silica tube was suspended from the ceiling by fine copper wires. The core size of the heating unit was then reduced by inserting plugs of insulating brick into each end which effectively made a heating zone of 3 1/2 inches in length and 3 inches in diameter.

VI. OPERATING CHARACTERISTICS

The completed furnace could operate at the following conditions. The heating zone could be varied from 12 inches long to less than 1 inch long by changing the size of the insulating brick plugs in the ends of the furnace core. The temperature of the heating unit could be varied from room temperature to at least 1400°F. with a control of ± 10°F. The heating unit could be made to travel along the tube at rates of 0.90, 1.43, 2.64, 3.60, 4.00, 5.72, 10.56 and 16.00 inches per hour by changing the belts and pulleys in the drive train.

APPENDIX B

APPENDIX B

CONSTRUCTION OF THE ETCH-CUTTER

The necessity of cutting indium specimens without recrystallization required the construction of an etch cutter. The etch-cutter constructed for this purpose was copied in its more important details from the design of Yamamoto and Watanabe.[9]

Most of the parts of the cutter were made of polyethylene plastic which is resistant to acid attack. The only exceptions were two brass shafts and numerous brass screws and other fasteners used to hold the assembly together. In most cases the brass components were coated with paraffin, however, to prevent their corrosion.

Figure 36 is a sketch of the basic design of the etch-cutter less the polyethylene breakers used to hold the acid, the electrical connections and the bracing needed for rigidity. For the general location of these items, see Figure 37 which is a photograph of the complete etch-cutter. The operation of the etch-cutter is as follows: the thread drum, B, with a reciprocating motion imparted to it by drive wheel, G, auxiliary drive wheel, H, and drive link, K, pulls a Saran, plastic thread, C, around rollers, D, and over specimen, E. The acid for the etching is supplied from polyethylene beakers placed so that the bottom rollers and the thread passing around them are immersed in the acid. The power to drive the auxiliary shaft is obtained through a variable speed torque converter from a 1/12 H.P. A.C. electric motor. Provision for positioning the specimen is provided by the goniometer, F, to which

[9] Yamamoto and Watanabe, op. cit., p. 233.

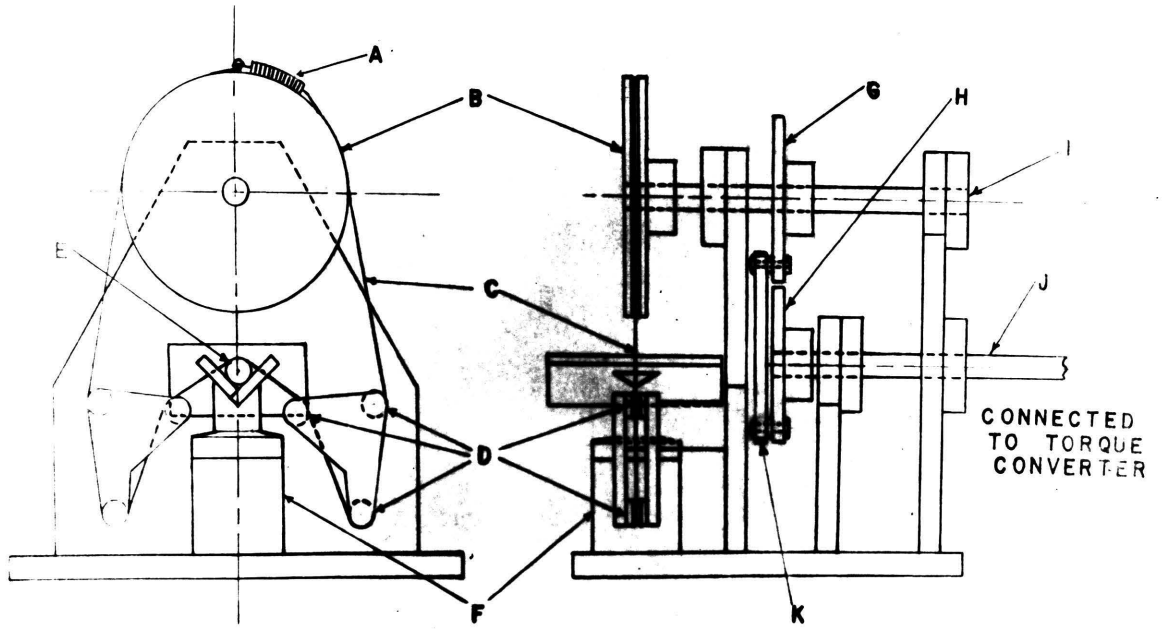

Figure 36. Sketch of etch-cutter.

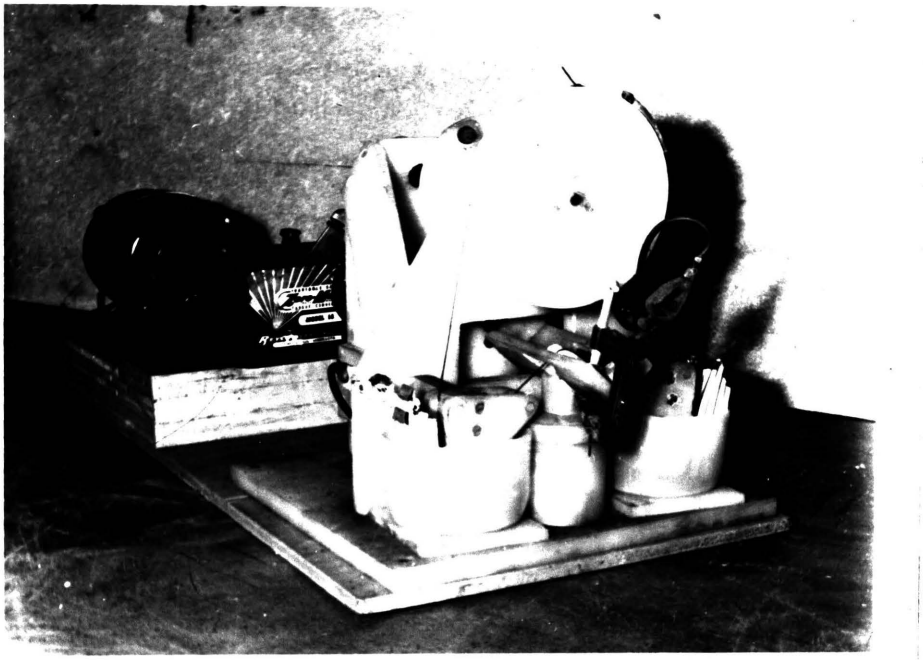

Figure 37. Complete etch-cutter as used for indium.

the specimen is secured by a small C-clamp.

The incorporation of an electrolytic reaction to assist the cutting was copied from Piontelli, Rivolta and Sternheim.[91] To accomplish this two alligator clips were employed to hold a platinum electrode in each bath as cathodes and a flexible wire with another clip was fastened to the specimen for the anode. A toggle switch and a power line to the 230 V.D.C. power source completed the arrangement.

Three variables had to be controlled. (1) speed of thread travel (2) acid to be used, and (3) thread tension. The speed of thread travel can be easily regulated by the number of cycles that the drum makes which, in turn, is controlled by the variable speed torque converter. High speeds are to be avoided since they are both unnecessary and destructive to the equipment. As to the acid used for the etching, trial and error methods are best for making the most suitable choice. Thread tension is controlled by the length of the thread. A thread, 28 7/8 inches long was the best in this case. A gauge was made, by putting two tacks in a piece of wood 28 7/8 inches apart, to insure the use of the same length of thread at all times. Of course the thread tension decreases as the cut progresses down through the specimen because of the shorter path of travel and stretching of the thread. A longer spring would probably help adjust the tension and keep it more constant as the cut progressed.

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[91] Piontelli, Rivolta and Sternheim, loc. cit.

VITA

The author was born September 3, 1927 at Grand Haven, Michigan. He attended Nunica Elementary and Coopersville Public High School. He received a Bachelor of Science Degree in Metallurgical Engineering from the Michigan College of Mining and Technology in March, 1950. From September, 1950 to September, 1952, he served with the Army Engineers, and from December, 1952 to June, 1954, he was employed with the AC Spark Plug Division of General Motors. He entered the Missouri School of Mines and Metallurgy in 1954 and received a Master of Science Degree in Metallurgical Engineering from that school in June, 1955. He was appointed as a Graduate Assistant in Metallurgical Engineering in September, 1957.